Ab Initio Methods in Quantum Chemistry—I
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EFFECTIVE HAMILTONIANS AND PSEUDO-OPERATORS AS TOOLS FOR RIGOROUS MODELLING

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I. INTRODUCTION

Progress in the reliability of quantum-chemical *ab initio* techniques has been so impressive that the quantum-chemical calculations are sometimes proposed to chemists as a 'new spectroscopy'; in many cases they can actually provide information more direct than (and almost as reliable as) the experimental spectroscopies. This is especially true for problems concerning the possible existence and structure of transient polyatomic small molecules, the order of magnitude of activation energies, and so on. This increasing efficiency in the prediction ability of these instruments is largely due to technological progress in computers (i.e. to an exogenic factor), but it has proceeded through the development of mathematically efficient and physically relevant algorithms, which required a new scientific profile for quantum

chemists. Their pride and hopeful prospects are thus partly grounded. One should, however, point out two types of problems.

A. Quantum Chemistry as a Science or a Technology?

The numerical efficiency of black boxes giving more and more precise numbers to experimentalists is a technological goal; it actually exhibits a tendency to transform this field into a numerical spectrometer, but it defines neither a scientific field nor a scientific demand. The physical sciences are (or were?) essentially deductive, i.e. they started from general principles and, through a series of simplifying and reasonable assumptions, they were able to derive—mostly through analytical models—some laws, trends, orders of magnitude, etc., in an explicit way. Computational black boxes deliver the desired energy, and as a by-product, a wavefunction spread on thousands of determinants, which can neither be read nor understood, and does not even offer a possible way for an *a posteriori* rationalization. The information becomes so vast that it becomes useless. If one still believes that science must bring some explanation or derivation, reduction of information must be considered as a desirable task. The present contribution assumes that the rational reduction of information represents an essential goal for *understanding* physics and chemistry, and this must proceed through physically grounded simplified schemes.

B. Reduction of Information: Two Essential Tools

The present review is devoted to two main approaches that may lead in a controlled way from the exact Hamiltonian to simplified Hamiltonians, which are more easy to handle and on which deductive derivations may be easier to draw. One approach proceeds through *projections* of some exact wavefunctions into a relevant reduced subspace and leads to the *effective Hamiltonian* methodology. The techniques will be described in Section II.A, and their applications in Section III. The other procedure may be considered as a *simulation* of the considered exact Hamiltonian by a simpler Hamiltonian, the efficiency of the simulation being measured through a reduced distance, taken on a small subspace. This procedure, described in Section II.B, leads to the definition of pseudo-Hamiltonians or pseudo-operators. The corresponding applications are reviewed in Section IV.

C. Terminology: a Proposal

Despite the large confusion in the terminology existing in this field (to which the authors have also contributed), we propose for the future the following vocabulary:

1. The term 'effective Hamiltonian' should be used for Hamiltonians obtained

by projections of some exact wavefunctions onto a finite model space. The corresponding theory is well established and the practical (perturbative or not) procedures are numerous and well documented.

2. The term 'pseudo-Hamiltonian' should be used when they are obtained through simulation techniques, i.e. minimization of the distance between the exact and pseudo-operators in a reduced subspace.

The term 'model Hamiltonian' is more general. From this point of view the 'effective Hamiltonians' and 'pseudo-Hamiltonians' could also be considered as 'model Hamiltonians'. However, for clarity, we suggest that the term 'model Hamiltonian' should be used when some simplified form of an approximate Hamiltonian has been guessed from a preliminary physical analysis. In contrast with the 'effective Hamiltonians' and the 'pseudo-Hamiltonians' that can be obtained by means of well defined mathematical procedures, the 'model Hamiltonians' are generally parametrized from experiment. They would involve the semi-empirical Hamiltonians of quantum chemistry and solid-state physics (Hückel, Hubbard, Pariser–Parr–Pople (PPP),...).

D. Desirable Simplifications in Quantum Chemistry

Modelling involves a reduction or a simplification of the problem. This reduction may concern:

1. The number of particles of the problem. This is the scope of π theories for conjugated systems and valence Hamiltonians more generally, but other reductions are conceivable.
2. The basis set of atomic orbitals (AO) in which the problem is supposed to be treated. All *ab initio* calculations use projected Hamiltonians since they work in finite basis sets, of course, solving

$$P_S H P_S \psi_S^m = E_S \psi_S^m$$

where P_S is the projector onto the space of determinants built in the considered AO basis set. But one may also try to build 'effective' Hamiltonians, different from the exact one, working only in a small basis set, but with modified operators giving better energies and wavefunctions than the previously defined E_S^m and ψ_S^m. This strategy is the one followed by K. Freed and coworkers in a series of papers, discussed later, which also try to achieve the previously mentioned goal (reduction of the number of particles).
3. The number of N-electron configurations (or determinants) in which one would like to treat the problem. Instead of handling the huge number of configurations which span the Hamiltonian in a finite basis set (full configuration interaction (CI)), one may wish to explain the behaviour of a few solutions in terms of a few leading configurations only, without losing the quality of the energetic information. There exist two main examples of this strategy,

a. one is the interpretation of curve crossings between molecular potential energy surfaces and their diabatic description in terms of dominant configurations,
b. the other concerns the Heisenberg Hamiltonians, which only treat neutral situations in minimal basis sets in such a way that they deliver correct energies, despite the lack of inclusion of ionic states.

One should notice that point 2. implies a reduction of the number of determinants, but point 3 is not reducible to point 2.

4. The relativistic molecular calculations are very difficult as long as they keep four-component wavefunctions according to the Dirac theory. The reduction to a two-component Pauli-like formalism within the effective Hamiltonian theory allows one to perform standard relativistic variational calculations.
5. As a basically different approach, one may consider the simplification of the Hamiltonian, for instance its analytical form. One may try to build a purely monoelectronic Hamiltonian that is 'as close as possible' in some aspects to the exact (bielectronic) Hamiltonian; for instance, which reproduces as closely as possible the Fock monoelectronic energies obtained from the exact Hamiltonian, or the total energy and its changes.

E. Simplification and Efficiency Overlap

As a concluding remark, we would like to stress the fact that effort to find efficient and physically grounded simplified Hamiltonians is not only the answer to a desire for interpretation, it is also a valuable technical tool for the treatment of large systems, since the N dependences of *ab initio* quantum-chemical algorithms are still prohibitive and forbid the treatment of large polyatomic systems, despite the expected progress in computational facilities. Happily enough, the desire for simplification of the information, the desire for understanding, is not at odds with research into numerical efficiency. This is clear for the treatment of large systems, but it is even true for the heavy *ab initio* techniques concerning small systems: techniques that express the CI results in terms of more convenient nearly diabatic pictures rest on the effective Hamiltonian theory. They are less expensive than the usual adiabatic approaches and they may help to solve numerical accuracy problems in the treatment of excited states in large CI approaches, as shown in Section III.B.

II. MATHEMATICAL TOOLS

A. Effective Hamiltonians by Projection Techniques[1-3]

1. The Model Space

The concept of *model space* plays a central role in the theory of effective Hamiltonians.[2] It is a finite N_m-dimensional subspace S_0 of the entire Hilbert

space. Physics will further be projected in this model space. Its orthogonal complement is the *outer space* $S_0^\perp$. The orthogonal projection operators associated with S_0 and $S_0^\perp$ are P_0 and Q_0, respectively:

$$P_0 = \sum_{m=1}^{N_m} |m\rangle\langle m| \qquad Q_0 = \sum_{\alpha} |\alpha\rangle\langle\alpha| \qquad P_0 + Q_0 = 1 \tag{1}$$

The Latin letters $m, n, \ldots$ and Greek letters $\alpha, \beta, \ldots$ will label functions of the model space and the outer space, respectively.

It is also useful to consider an N_m-dimensional subspace S spanned by N_m exact solutions ψ_m of the exact Hamiltonian H. These solutions will correspond to the part of the spectrum in which we are interested. The orthogonal complement of S is denoted $S^\perp$. The orthogonal projectors associated with S and $S^\perp$ are P and Q:

$$P = \sum_{m=1}^{N_m} |\psi_m\rangle\langle\psi_m| \qquad Q = \sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha| \qquad P + Q = 1 \tag{2}$$

The ψ_α are the exact solutions of H belonging to $S^\perp$. The projections Φ_m of the exact solutions ψ_m into the model space play a central role in the theory:

$$\psi_m \in S \rightleftharpoons \Phi_m = P_0\psi_m \in S_0 \tag{3}$$

Relation (3) establishes a one-to-one correspondence between S and S_0. The projected wavefunctions Φ_m are usually not orthogonal and the corresponding bi-orthogonal states in S_0, noted $\Phi_m^\perp$, have the usual properties:

$$\langle\Phi_m^\perp|\Phi_n\rangle = \delta_{mn} \qquad \sum_{m=1}^{N_m} |\Phi_m\rangle\langle\Phi_m^\perp| = P_0 \tag{4}$$

2. *The Feschbach–Löwdin Hamiltonian*[4-6]

Let us consider an exact eigenstate of energy E:

$$H\psi = E\psi \tag{5}$$

This state may be non-degenerate or degenerate. Using the projections operators P_0 and Q_0, Eq. (5) can be partitioned according to (partitioning technique)

$$\begin{aligned} P_0HP_0\psi + P_0HQ_0\psi &= EP_0\psi \\ Q_0HP_0\psi + Q_0HQ_0\psi &= EQ_0\psi \end{aligned} \tag{6}$$

It can easily be seen from (6) that the projection $\Phi = P_0\psi$ of ψ in the model space is a solution of

$$H^{\text{eff}}\Phi = E\Phi \tag{7}$$

where

$$H^{\text{eff}} = P_0 H P_0 + P_0 H \frac{Q_0}{E - H} H P_0 \tag{8}$$

$Q_0/(E-H)$ is a reduced resolvent defined in the outer space. H^{eff} can also be written in the form

$$H^{\text{eff}} = P_0 H P_0 + P_0 V \frac{Q_0}{E - H} V P_0 \tag{9}$$

where the coupling operators $P_0 H Q_0$ and $Q_0 H P_0$ have been denoted $P_0 V Q_0$ and $Q_0 V P_0$, respectively.

H^{eff} given by (8) or (9) is an effective Hamiltonian which possesses the exact eigenenergy E and the corresponding wavefunction $\Phi = P_0 \psi$. It can also be written in the form

$$H^{\text{eff}} = P_0 H \Omega_E \tag{10}$$

where

$$\Omega_E = P_0 + \frac{Q_0}{E - H} V P_0 \tag{11}$$

Ω_E is a *wave operator*, parametrized by the exact energy E, which has the basic property of generating the exact wavefunction when acting on its projection in the model space:

$$\Omega_E \Phi = \Omega_E P_0 \psi = \psi \tag{12}$$

Figure 1 gives an illustration of the correspondence between ψ and Φ by means of P_0 and Ω_E.

Despite its apparent simplicity the Feschbach–Löwdin Hamiltonian suffers from a severe limitation: it is relevant for only one energy level and there are as many H^{eff} as energies. This limitation pleads in favour of a energy-independent formalism that will now be presented throughout this section.

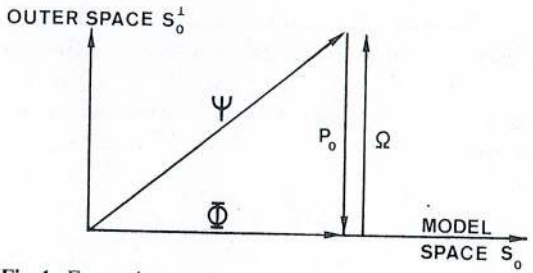


Fig. 1. From the exact wavefunction ψ to the projected wavefunction Φ and back from Φ to ψ by the wave operator Ω.

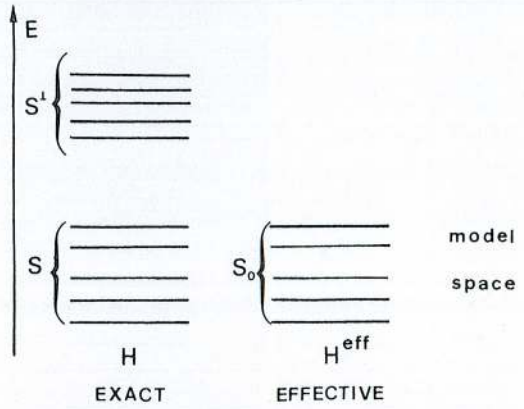


Fig. 2. The exact Hamiltonian H and the effective Hamiltonian have the same eigenenergies in the subspaces S and S_0, respectively.

3. *The Bloch and des Cloizeaux Effective Hamiltonians*[7,8]

The basic idea is to pass from the exact Hamiltonian H to an effective Hamiltonian whose eigenenergies coincide within a subset of the eigenenergies of H (Fig. 2). In this approach all the information on the other eigenenergies of H is lost. The theory can easily be derived from the basic equation[9]

$$H\Omega = \Omega H^{\text{eff}} \tag{13}$$

where H^{eff} is an effective Hamiltonian defined in the N_m-dimensional model space S_0 and Ω is the associated *wave operator* acting in the model space:

$$\Omega = \Omega P_0 \tag{14}$$

Equation (13) shows immediately that if Φ_m is an eigensolution of energy E_m then

$$\psi_m = \Omega \Phi_m \tag{15}$$

is an exact solution of H. Equation (15) expresses a one-to-one correspondence between the N_m solutions of H^{eff} which span the model space S_0 and N_m exact solutions of H which span the relevant physical space S. Hereafter this *a priori* unknown space will be called the *target space*. Equation (13) appears as a simple generalization of the ordinary Schrödinger equation for one state (Eq. (5)) to an operator equation for handling simultaneously N_m states. In this equation the unknown quantities are Ω and H^{eff}. Equation (13) has many solutions and the most meaningful ones were identified in the 1950s by Okubo, Bloch and des Cloizeaux.[7,8,10] The solution obtained by Bloch in the framework of perturbation theory now appears as the most fundamental in the theory of effective Hamiltonians.

The Bloch formalism is determined in a natural way by choosing that the N_m solutions of H^{eff} in the model space must be the projections in the model space of N_m exact solutions ψ_m spanning the target space S:

$$H^{\text{eff}}\Phi_m = E_m\Phi_m \qquad \Phi_m = P_0\psi_m \qquad m = 1, 2, \ldots, N_m \tag{16}$$

The wave operator associated with the solutions can be written in compact form as[11,12]

$$\Omega = P(P_0PP_0)^{-1} \tag{17}$$

It is worth noting that Ω depends only on the projectors P and P_0. From (17) it can immediately be checked that Ω has the following properties:

$$P_0\Omega = P_0 \qquad \Omega^2 = \Omega \qquad \Omega^\dagger \neq \Omega \tag{18}$$

The first one is associated with the so-called intermediate normalization and the second one means that Ω is a non-orthogonal projection operator. From Ω one can obtain the expression for the projector P:

$$P = \Omega(\Omega^\dagger\Omega)^{-1}\Omega^\dagger \tag{19}$$

Multiplying both sides of Eq. (13) on the left by P_0 and using the intermediate normalization property leads to the Bloch effective Hamiltonian:

$$H^{\text{eff}} = P_0H\Omega \tag{20}$$

the spectral decomposition of which is

$$H^{\text{eff}} = \sum_{m=1}^{N_m} E_m|\Phi_m\rangle\langle\Phi_m| \tag{21}$$

Introducing the above expression for H^{eff} in (13) leads to the basic wave operator equation:[13]

$$H\Omega = \Omega H\Omega \tag{22}$$

This equation is a generalization of an equation previously found by Bloch and generalized by Lindgren.[14] Solving the operator equation (22) appears as the main task in the Bloch theory of effective Hamiltonians since H^{eff} can immediately be deduced from Ω by means of (20). It will also be shown below that the wave operator Ω plays a fundamental role in the whole theory of effective Hamiltonians.

The Bloch Hamiltonian (20) is non-Hermitian since its solutions are the projections in the model space of exact solutions of the exact Hamiltonian. This can also be seen directly from expressions (17) and (20). The hermitization of the Bloch Hamiltonian can easily be obtained by requiring that the solutions of the new effective Hamiltonian are the symmetrically orthogonalized solutions of the Bloch Hamiltonian:[3]

$$H^{\text{eff}}(\text{des Cloizeaux}) = (\Omega^\dagger\Omega)^{1/2}H^{\text{eff}}(\text{Bloch})\,(\Omega^\dagger\Omega)^{-1/2} \tag{23}$$

This expression does not appear to be Hermitian, but in fact it is. From (17) one obtains

$$\Omega^{\dagger}\Omega = (P_0 P P_0)^{-1} \tag{24}$$

and (23) becomes

$$H^{\text{eff}}(\text{des Cloizeaux}) = (P_0 P P_0)^{-1/2} P H P (P_0 P P_0)^{-1/2} \tag{25}$$

This last expression is obviously Hermitian and its spectral decomposition is

$$H^{\text{eff}}(\text{des Cloizeaux}) = \sum_{m=1}^{N_m} E_m |\Phi'_m\rangle\langle\Phi'_m| \tag{26}$$

where Φ'_m is defined in eq. (28).

a. The non-orthogonality problem

For a deeper understanding of the non-Hermitian Bloch and Hermitian des Cloizeaux formalisms, it is useful to consider the expressions of Φ_m and Φ'_m appearing in (21) and (26):

$$\Phi_m^{\perp} = \sum_{n=1}^{N_m} (S^{-1})_{mn} \Phi_n \tag{27}$$

$$\Phi'_m = \sum_{n=1}^{N_m} (S^{-1/2})_{mn} \Phi_n \tag{28}$$

S being the overlap matrix between the Φ_m, and $(S^{-1})_{mn}$ and $(S^{-1/2})_{mn}$ represent the (m, n) matrix element of the matrices S^{-1} and $S^{-1/2}$, respectively. When this matrix is almost unity, the functions Φ_m, $\Phi_m^{\perp}$ and Φ'_m look like the exact wavefunction ψ_m and the Bloch effective Hamiltonian is almost Hermitian. In contrast, when the physical content of at least one projected wavefunction $\Phi_m \equiv P_0 \psi_m$ is far from the exact wavefunction ψ_m or, expressed in mathematical terms, when at least one diagonal matrix element of the overlap matrix S is small with respect to unity, then the matrices $S^{-1/2}$ and S^{-1} become singular. The bi-orthogonal wavefunctions Φ_m become meaningless and the Bloch Hamiltonian (21), the spectral decomposition of which implies the $\Phi_m^{\perp}$, becomes strongly non-orthogonal. Many possibilities can be considered for facing up to these difficulties.

First one can build up other effective Hamiltonians based on hierarchized orthogonalization procedures. The Gram–Schmidt procedure is recommended if one starts from the best projected wavefunctions of the bottom of the spectrum. Thus one can obtain a quite reliable effective Hamiltonian with well behaved wavefunctions and good transferability properties (see Section III.D.2). The main drawback of this approach is that the Gram–Schmidt method, which involves triangular matrices, does not lead to simple analytical expressions for perturbation expansions. A partial solution to these limitations is brought about by the new concept of *intermediate Hamiltonian*,

which will be presented in Section III.A.6. One can easily obtain almost Hermitian Hamiltonians that can easily be expanded by standard perturbation theory but with the new limitation that only one part of their roots are exact eigenenergies of the full Hamiltonian.

Another way of handling the non-orthogonality problem was suggested by Kato more than 30 years ago.[15] By means of (17) and (20), the eigenvalue equation (16) can be transformed into[16]

$$(\mathscr{H} - E\mathscr{I})\Phi_m^{\perp} = 0 \qquad m = 1, 2, \ldots, N_m \tag{29}$$

where

$$\mathscr{H} = P_0 P H P_0 \qquad \text{and} \qquad \mathscr{I} = P_0 P P_0 \tag{30}$$

The 'effective' Hamiltonian $\mathscr{H}$ and the metric (or overlap) operator $\mathscr{I}$ are Hermitian. The equation looks like those frequently used for solving the Schrödinger equation by means of a non-orthogonal basis set, as for instance in valence-bond (VB) theory. The operators $\mathscr{H}$ and $\mathscr{I}$ seem to have interesting transferability potentialities but up to now they do not seem to have been used for practical investigations. A more general approach has recently been given by Suzuki.[17,18]

4. *Solutions of the Bloch Equation*

Im most cases the wave operator cannot be determined from expression (17) since the projector P on the target space is generally unknown. Then one has to solve directly the wave operator equation (22). Let us first introduce a *reduced wave operator* X by using the intermediate normalization and writing Ω as

$$\Omega = (P_0 + Q_0)\Omega = P_0 + X \tag{31}$$

X is a transition operator that couples the model space and the outer space:

$$X = Q_0 X P_0 \tag{32}$$

This operator had previously been denoted χ by Lindgren[2] and ω by Suzuki.[17] A lower-case letter seems a good choice for the reduced operator, keeping the capital letter Ω for the full operator. However, we prefer to use the notation X, which clearly indicates that X is the unknown quantity.[13] We will see below that an operator equation for X can be put in the form $F(X) = 0$, which suggests that this equation could be solved in close analogy with the standard methods of resolution of an ordinary algebraic equation $f(x) = 0$.

An equation for X, originally given by Okubo, can easily be obtained by multiplying both sides of Eq. (22) on the left by Q_0:

$$Q_0 H(P_0 + X) = X H(P_0 + X) \tag{33}$$

This equation can be written in the form

$$F(X) = 0 \qquad \text{with} \qquad F(X) \equiv Q_0(1 - X)H(1 + X) \tag{34}$$

Equation (34) can be solved by the standard iterative methods, which can be classified according to their rates of convergence: linear, quadratic or quasi-quadratic.[19] The true quadratic methods, which are analogous to the Newton–Raphson procedure for ordinary algebraic equations, would involve the inversion of huge superoperators acting in the linear space of all transition operators coupling the model space and the outer space. These inversions would be as difficult as the direct resolution of the Schrödinger equation for the exact Hamiltonian. For many-body applications the inversion of these operators is performed in an approximate way by methods similar to the partial infinite summation techniques of many-body theory. The linear methods are also attractive for a first approach since they are closely associated with the standard perturbation theory which finds in this approach its rigorous foundation.[13,20,21]

The simplest way for deriving approximate compact expressions for X is to introduce an energy parameter E_0 approximately equal to the mean value of the eigenenergies of H^{eff}. Subtracting E_0X from both sides of Eq. (33) gives.

$$Q_0(E_0 - H)X = Q_0HP_0 - XH(P_0 + X) + E_0X \tag{35}$$

which can be put in the form

$$X = f(X) \qquad \text{with}$$

$$f(X) \equiv \frac{Q_0}{E_0 - H}VP_0 + \frac{Q_0}{E_0 - H}[X(E_0 - H) - XVX]P_0 \tag{36}$$

In this last expression we have again used the perturbation notation $Q_0VP_0 \equiv Q_0HP_0$ and $P_0VQ_0 \equiv P_0HQ_0$. The solution of Eq. (36) can immediately be found by iteration:

$$X^{(0)} = 0 \tag{37a}$$

$$X^{(1)} = f(X^{(0)}) = \frac{Q_0}{E_0 - H}VP_0 \tag{37b}$$

$$\vdots \qquad \vdots$$

$$X^{(n+1)} = f(X^n) \tag{37c}$$

The expression (36) of $f(X)$ indicates that the convergence properties of the iterative procedure will depend on the smallness of the coupling operator and on $P_0(E_0 - H)P_0$ defined in the model space with respect to the reduced Green's operator $Q_0/E_0 - H$. Keeping terms up to the second iteraction gives

$$X = \frac{Q_0}{E_0 - H}VP_0 + \frac{Q_0}{(E_0 - H)^2}VP_0(E_0 - H)P_0$$

$$- \frac{Q_0}{(E_0 - H)^2}VP_0V\frac{Q_0}{E_0 - H}VP_0 + \cdots \tag{38}$$

This expression is more useful for general discussions than for practical applications since it would require knowledge of the reduced Green's operator $Q_0/E_0 - H$. However, it must be noted that in relativity the very particular structure of the Dirac equation allows direct determination of $Q_0/E_0 - H$ (see Section III.A).

a. Solutions by perturbation

The exact Hamiltonian is split into an unperturbed zero-order Hamiltonian and a perturbation:

$$H = H_0 + V \tag{39}$$

where

$$H_0 = \sum_{m=1}^{N_m} E_m^0 |m\rangle\langle m| + \sum_{\alpha} E_\alpha^0 |\alpha\rangle\langle\alpha| \tag{40}$$

With (39) and (40), Eq. (33) can be transformed into the commutator equation

$$[X, H_0] = Q_0(1 - X)V(1 + X)P_0 \tag{41}$$

which can be put in the form of an implicit equation for X:

$$X = \sum_{m=1}^{N_m} \frac{Q_0}{E_m^0 - H_0}(1 - X)V(1 + X)P_m \tag{42}$$

In Eq. (42) $P_m = |m\rangle\langle m|$ is the projector associated with the unperturbed eigensolution $|m\rangle$ of H_0. Equation (42) can immediately be solved by successive iterations, which provide the perturbation expansion of X in powers of V:

$$X = \sum_{k=1}^{\infty} X^{(k)} \tag{43}$$

$$X^{(1)} = \sum_{m=1}^{N_m} \frac{Q_0}{E_m^0 - H_0} V P_m \tag{44}$$

$$X^{(2)} = \sum_{m=1}^{N_m} \frac{Q_0}{E_m^0 - H_0} V \frac{Q_0}{E_m^0 - H_0} V P_m - \sum_{m,n=1}^{N_m} \frac{Q_0}{(E_m^0 - H_0)(E_n^0 - H_0)} V P_m V P_n + \cdots \tag{45}$$

The choice of a degenerate unperturbed Hamiltonian in the model space greatly simplifies the perturbation expansion of X. With the assumption that $E_1^0 = E_2^0 = \cdots = E_m^0 = E^0$, expressions (44) and (45) reduce to

$$X^{(1)} = \frac{Q_0}{E_0 - H_0} V P_0 \tag{46}$$

$$X^{(2)} = \frac{Q_0}{E_0 - H_0} V \frac{Q_0}{E_0 - H_0} V P_0 - \frac{Q_0}{(E_0 - H_0)^2} V P_0 V P_0 \tag{47}$$

Let us now introduce a more compact notation, which leads to the expansion

$$\begin{aligned} \Omega &= P_0 + X = \sum_{n=0}^{\infty} \Omega^{(n)} \\ \Omega^{(0)} &= P_0 \\ \Omega^{(1)} &= g V P_0 \\ &\vdots \quad \vdots \\ \Omega^{(n)} &= g\left(V\Omega^{(n-1)} - \sum_{k=1}^{n-1} \Omega^{(k)} V \Omega^{(n-k-1)} \right) \end{aligned} \tag{48}$$

where

$$g = \frac{Q_0}{E_0 - H_0} = \sum_{\alpha} \frac{|\alpha\rangle\langle\alpha|}{E_0 - E_\alpha^0} \tag{49}$$

The expansion of Ω immediately generates the perturbation expansion of the Bloch effective Hamiltonian:

$$\begin{aligned} H^{\text{eff}} &= \sum_{n=0}^{\infty} H_{\text{eff}}^{(n)} \\ H_{\text{eff}}^{(0)} &= P_0 H_0 \\ H_{\text{eff}}^{(1)} &= P_0 V P_0 \\ H_{\text{eff}}^{(2)} &= P_0 V g V P_0 \\ &\vdots \quad \vdots \\ H_{\text{eff}}^{(n)} &= P_0 V \Omega^{(n-1)} \end{aligned} \tag{50}$$

Expansion of H^{eff} up to third order can be found in Lindgren.[2] Very often the perturbation expansion diverges and the first few terms give only an approximation of the true solution (asymptotic convergence). Compact perturbation expansions of the wave operator have recently been given by Suzuki for both the degenerate and quasi-degenerate cases.[22]

b. The choice of the target space

The above theory of the Bloch effective Hamiltonian was mainly based on two finite N_m-dimensional subspaces: the model space S_0 and the target space S, with projectors P_0 and P respectively. There is no difficulty in choosing the model space on which the reduced quantum information will be projected. The definition of the target space is not so obvious. If the energy levels associated

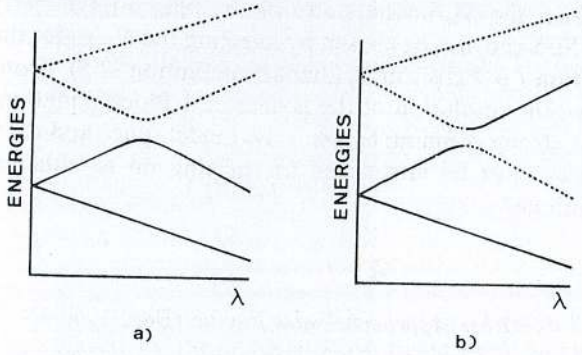


Fig. 3. Eigenenergies of a four-dimensional Hamiltonian (full curves and dotted curves). The two eigenenergies of H^{eff} (full curves) are represented as a function of an arbitrary parameter λ (for example the internuclear distance in a diatomic molecule). Cases (a) and (b) correspond to the adiabatic and diabatic definitions of H^{eff}, respectively.

. with the model space are well separated from all the other energies of the spectrum, ore more precisely, in terms of perturbation, if there is a small coupling between the states of the model space S_0 and those of the outer space $S_0^{\perp}$ for the exact Hamiltonian, then there is no ambiguity in identifying the target space. The resolution of the generalized Bloch equation (22) by means of the techniques of Section II.A.4 will always lead to a stable subspace S. The definition of S is not so obvious when there is a strong coupling between S_0 and $S_0^{\perp}$. This occurs for example in the presence of an ionic molecular intruder state in the model space of neutral states[13] (see Sections III.C and III.D). This situation is illustrated in Fig. 3 where one considers two possible ways of defining S from S_0 for a two-dimensional effective Hamiltonian. In case (a) there is a rapid change in the second eigenvector, the component of which in the model space vanishes asymptotically, making the wave operator undefined. (The operator P_0PP_0 is singular and the inversion occurring in equation (2.17) becomes impossible.) In contrast, in case (b), the eigenvalues and eigenvectors are discontinuous whereas the physical content of S remains stable. This means that, for all values of parameter λ, the subspace S remains as similar as possible to the model subspace S_0. In both cases we are faced with discontinuities in the effective Hamiltonian either in the physical content of the solutions (case (a)) or in the energies (case(b)). These difficulties are partially solved by introducing the concept of intermediate Hamiltonian (Section II.A.6). From a mathematical point of view, any subspace made up of N_m exact solutions of H can be chosen as the target space but for physical purposes only two main criteria seem to be useful: the subspace S can be chosen from an energetic

criterion, taking the N_m lowest states of the relevant symmetry (adiabatic definition of S); S can also be chosen by selecting the N_m states that maximize their occupation $\langle\psi|P_0|\psi\rangle$ in S_0 (diabatic definition of S). From a practical point of view, the resolution of the generalized Bloch equation is unstable when there is strong coupling between the model space and the outer space. Special devices must be introduced for turning on to either adiabatic or diabatic solutions.

5. *Other Approaches and Further Developments*

The two basic effective Hamiltonians of Bloch and des Cloizeaux can also be obtained by means of similarity transformations, which reveals with deeper details the mathematical structure of the theory.[23-28] The exact Hamiltonian is first transformed by means of a similarity transformation:

$$\mathscr{H} = U^{-1}HU \tag{51}$$

U has an inverse but it is not required to be unitary. Various effective Hamiltonians can be obtained under the assumption that the transformation U decouples H within the model space and the outer space (Fig. 4):

$$\mathscr{H} = \underset{H^{\text{eff}}}{P_0\mathscr{H}P_0} + \underset{H^{\text{eff}\perp}}{Q_0\mathscr{H}Q_0} \tag{52}$$

The most basic transformation can be written as

$$U = P(P_0PP_0)^{-\nu} + Q(Q_0QQ_0)^{-\nu}$$
$$U^{-1} = (P_0PP_0)^{\nu-1}P + (Q_0QQ_0)^{\nu-1}Q \tag{53a}$$

where ν is a non-negative index.[13,26] It can easily be checked that the values

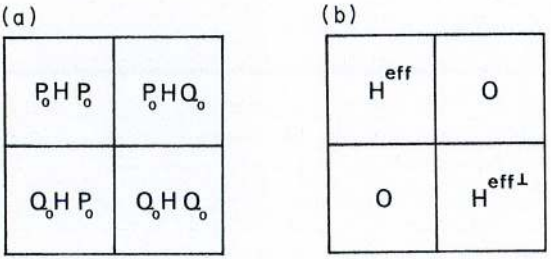


Fig. 4. (a) Matrix representation of H. (b) Matrix representation of H^{eff} and $H^{\text{eff}\perp}$. The projectors onto the model space S_0 and its orthogonal complement are P_0 and Q_0, respectively.

$v = 1$ and $v = \frac{1}{2}$ generate the Bloch and des Cloizeaux Hamiltonians. For $v = 1$

$$U(\text{Bloch}) = P(P_0PP_0)^{-1} + Q(Q_0QQ_0)^{-1} \tag{54a}$$

$$U^{-1}(\text{Bloch}) = P_0P + Q_0Q \tag{54b}$$

The Bloch U operator can also be written in the form

$$U(\text{Bloch}) = 1 + u \tag{55}$$

where

$$u = X - X^{\dagger} \tag{56}$$

u is an anti-Hermitian operator ($u^{\dagger} = -u$). Expression (56) emphasizes again the central role played by the reduced wave operator X in the theory of effective Hamiltonians. The value $v = \frac{1}{2}$ leads to the des Cloizeaux formalism

$$U(\text{des Cloizeaux}) = P(P_0PP_0)^{-1/2} + Q(Q_0QQ_0)^{-1/2} \tag{57}$$

This operator is obviously Hermitian:

$$\begin{aligned} U^{-1}(\text{des Cloizeaux}) &= U^{\dagger}(\text{des Cloizeaux}) \\ &= (P_0PP_0)^{-1/2}P + (Q_0QQ_0)^{-1/2}Q \end{aligned} \tag{58}$$

U of expression (57) can also formally be written as

$$U(\text{des Cloizeaux}) = (1+u)(1-u^2)^{-1/2} = \left(\frac{1+u}{1-u}\right)^{1/2} \tag{59}$$

It is sometimes useful for separability problems (i.e. size consistency) to introduce an exponential operator G by

$$U(\text{des Cloizeaux}) = e^{G} \tag{60}$$

G can be expressed as a simple analytical function of u[24,25,27]

$$G = \tanh^{-1} u \tag{61}$$

In the last few years the general theory of effective Hamiltonians has been reformulated by Kutzelnigg in the Fock space.[29–33] The use of creation and annihilation operators is supposed to simplify the calculation of quantities involving variation of the number of particles, such as ionization potentials or electron affinities. Up to now no specific applications have been published with this formalism, the practical efficiency of which is still to be established.

6. *Intermediate Hamiltonians*[34]

The discussions concerning the non-orthogonality problem (Section II.A.3) and the choice of the target space (Section II.A.4) have shown that the Bloch and des Cloizeaux effective Hamiltonians suffer from convergence difficulties especially in the presence of molecular intruder states that lead to discontinu-

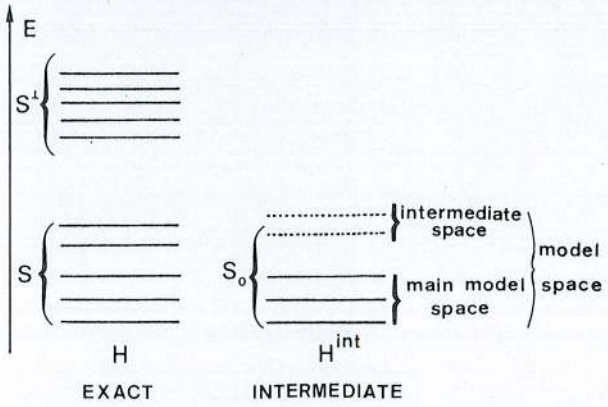


Fig. 5. The exact Hamiltonian H and the intermediate Hamiltonian H^{int} have the same eigenenergies in a subspace of S and in the main model subspace. Moreover, H^{int} also has approximate eigenenergies (dotted lines) in the intermediate subspace.

ities of their matrix elements as a function of internuclear distances. To combat these difficulties, the concept of an intermediate Hamiltonian has recently been proposed (Fig. 5).

The model space is split into an N_m-dimensional *main model space* and an N_i-dimensional *intermediate space* with projectors

$$P_m = \sum_{m=1}^{N_m} |m\rangle\langle m| \qquad P_i = \sum_{i=1}^{N_i} |i\rangle\langle i| \qquad P_m + P_i = P_0 \tag{62}$$

The *intermediate Hamiltonian*, denoted H^{int}, is defined in the $(N_m + N_i)$-dimensional model space. Among the $N_m + N_i$ eigenenergies of H^{int}, only N_m are exact eigenvalues of H. This loss of information on the energies is the price one has to pay for improving the hermiticity and the convergence properties of an intermediate Hamiltonian with respect to the previously described effective Hamiltonians.

The theory of intermediate Hamiltonians is based on the introduction of a new wave-like operator R. Then a large class of intermediate Hamiltonians can be written as

$$H^{\text{int}} = P_0 H R \tag{63}$$

with R fulfilling the condition

$$R\Omega = \Omega \tag{64}$$

Ω is the Bloch operator associated with the main model space. In close analogy with the Bloch theory, an equation for R can be chosen in the form

$$Q_0 H R = Q_0 \Omega H R \tag{65}$$

or more generally one can take

$$Q_0(E_0 - H)R = Q_0\Omega(E_0 - H)R \tag{66}$$

where E_0 is an unperturbed energy typically of the order of magnitude of the exact eigenenergies in the main model space. In Eq. (66) the operator R is weakly E_0-dependent. Equation (66) can be solved by perturbation theory. Assuming that H_0 is degenerate in the main model space:

$$H_0 = \sum_{m=1}^{N_m} E_0|m\rangle\langle m| + \sum_{i=1}^{N_i} E_i^0|i\rangle\langle i| + \sum_{\alpha} E_\alpha^0|\alpha\rangle\langle\alpha| \tag{67}$$

Eq. (66) can be written in the form

$$Q_0R = g(1-\Omega)VR \qquad g = \sum_{\alpha}\frac{|\alpha\rangle\langle\alpha|}{E_0 - E_\alpha^0} \tag{68}$$

Assuming that R still obeys the intermediate normalization, Eq. (68) leads to the perturbation expansion:

$$R = P_0 + Q_0R = \sum_{n=0}^{\infty} R^{(n)} \tag{69}$$

$$R^{(0)} = P_0$$

$$R^{(1)} = gVP_0$$

$$\vdots \qquad \vdots$$

$$R^{(n)} = g\left(VR^{(n-1)} - \sum_{k=1}^{n-1}\Omega^{(k)}VR^{(n-k-1)}\right)$$

The expansion of the intermediate Hamiltonian is obtained order by order from the expansion of R. Note that the expansions of H^{int} and H^{eff}(Bloch) coincide up to second order.

7. *Size-consistency Problems*[35-44]

The present review does not enter into the famous and fundamental question of size consistency in many-body problems. This problem is well clarified in non-degenerate perturbation theory through the linked cluster theorem and for other approximate algorithms for the calculation of the correlation energy of an N-electron system. The size-consistency properties of the (nearly) degenerate perturbation theories are not as easy to establish. Brandow[39] has demonstrated a generalized linked cluster theorem when the model space is a complete active space, i.e. when it involves all the determinants in which p molecular orbitals (MO) (the core) are always doubly occupied while q (active) MOs receive k electrons with all possible distributions of these k electrons among the q MOs. This is a strong limita-

tion. Diagrammatic expansions have also been proposed for general model spaces[41,42] (i.e. leaving the preceding restriction) but the diagrammatic factorization ensuring size consistency is not perfect. One should notice here a fundamental contradiction: the complete active space requirement frequently leads to very large and broad model spaces (spread in a large range of energies), i.e. to convergence problems and difficulties in defining a target space while it ensures the size consistency; in contrast, smaller (non-complete) model spaces may face size-consistency problems. One should notice, however, that the Heisenberg Hamiltonians (cf. Section III.D) are based on a very incomplete model space, and are perfectly size-consistent. The complete active space condition thus appears as a sufficient but non-necessary condition. Much work remains to be done in this field.

B. Pseudo-Hamiltonians by Simulation Techniques

The previously described effective Hamiltonians cannot give a direct solution to the general problem of modelling in quantum chemistry and atomic physics. They only provide finite matrices of numbers that can be diagonalized to obtain a finite number of exact eigenenergies. In a rather unphysical way, all the other eigenenergies are equal to zero. On the contrary, the empirical or semi-empirical Hamiltonians (Hückel, PPP) generally involve one- and two-body interactions which have a clear physical meaning. The spectrum of these model Hamiltonians is extended but most often only the lowest states are significant. For example, a CNDO-type (complete neglect of differential overlap) Hamiltonian describes only the ground and the first few valence excited states of a molecule. An attractive characteristic of these Hamiltonians is that they contain transferable potentials and interactions, such as, for example, the β parameter in the Hückel theory which characterizes the interaction between any two π-bonded carbon atoms. A severe limitation of these models, generally parametrized from experiment, is that their theoretical status and their range of applicability are not well defined. The purpose of this section is to show that theoretical approximate Hamiltonians or *pseudo-Hamiltonians* can easily be derived from first principles by rigorous simulation techniques. This technique will be presented in Section II.B.1. It will also be shown in a second step that the practical determination of pseudo-operators and pseudo-Hamiltonians generally requires an intermediate step with the knowledge of a *truncated Hamiltonian* that contains less information than the original exact Hamiltonian.

1. Simulation Techniques[45]

Starting from an exact Hamiltonian H, one looks for an approximate pseudo-Hamiltonian H^{ps} as close as possible to H. This can be achieved by

minimizing the distance between H^{ps} and H:

$$\| H^{ps} - H \|_{\text{minimum}} \tag{70}$$

In the following it is assumed that H and H^{ps} are Hermitian. Let us suppose that H is acting in a basis of orthonormalized states denoted $|I\rangle$. The simplest definition of the distance between H^{ps} and H is

$$\| H^{ps} - H \| = \left(\sum_{I,J} |\langle I | H^{ps} - H | J \rangle|^2 \right)^{1/2} \tag{71}$$

For most applications this definition of the distance is not relevant; if the distance was taken in $\mathscr{L}^2$, the distance would be infinite and since the determination of H^{ps} is not required to have the same quality for all states $|I\rangle$, a better definition of the distance requires a *reduced distance*:

$$\| H^{ps} - H \| = \left(\sum_{I,J} |\langle I | H^{ps} - H | J \rangle|^2 w_{IJ} \right)^{1/2} \tag{72}$$

where the w_{IJ} are real positive (or zero) weights. For the following, it is useful to introduce a scalar-product notation. The Hermitian scalar product between two operators A and B belonging to the vectorial space of all operators acting in the space of the states $|I\rangle$ is defined by

$$(A|B) = \sum_{I,J} \langle I | A^{\dagger} | J \rangle \langle J | B | I \rangle w_{IJ} \tag{73a}$$

$$(A|B) = (B|A)^* \tag{73b}$$

With this notation the reduced distance (72) can be expressed as the square root of the scalar product of $H^{ps} - H$ with itself:

$$\| H^{ps} - H \| = (H^{ps} - H | H^{ps} - H)^{1/2} \tag{74}$$

and condition (70) becomes

$$(H^{ps} - H | H^{ps} - H)_{\text{minimum}} \tag{75}$$

Very often the pseudo-Hamiltonian can be written in the form of a linear combination of *a priori* known operators:

$$H^{ps} = \sum_i C_i A_i \tag{76}$$

The operators A_i may also depend on non-linear coefficients. In all cases the best choice for the non-linear and linear coefficients C_i is obtained by minimizing the distance between H and H^{ps}. According to the usual Fourier techniques, the minimization in (75) with respect to the coefficients C_i, assumed to be real, leads to the linear system of equations:

$$(A_i | H) = \sum_j (A_i | A_j) C_i \tag{77}$$

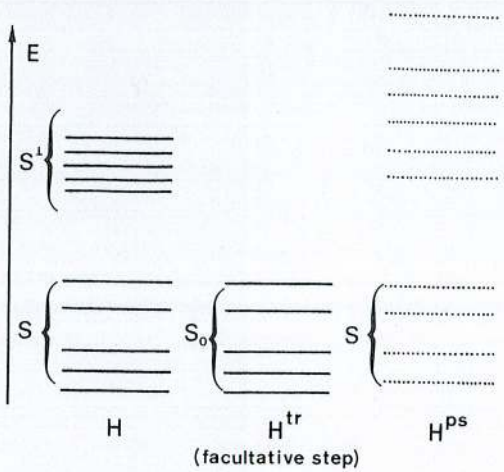


Fig. 6. The exact Hamiltonian H and the pseudo-Hamiltonian have approximately the same eigenenergies in the subspaces S and S', respectively H^{tr} having exact energies and truncated wave functions.

If the operators A_i are orthonormal,

$$(A_i|A_j) = \delta_{ij} \tag{78}$$

the resolution of (77) gives immediately

$$C_i = (A_i|H) \tag{79}$$

In most applications one is only interested in an accurate description of the bottom of the spectrum (Fig. 6). The previously undetermined states $|I\rangle$ become the exact solutions of H and the N_m lowest solutions define a subspace S previously called the target space. The projectors associated with S and its orthogonal complement are denoted P and Q, respectively. H^{ps} is now characterized by the requirement that H^{ps} and H have almost the same matrix elements in S and that there is almost no coupling between S and $S^{\perp}$. This implies that

$$w_{IJ} = \begin{cases} 1 & \text{if } I, J \in S \\ 0 & \text{if } J \in S^{\perp} \end{cases} \tag{80}$$

The reduced distance (72) can now be written as a partial trace:

$$\| H^{ps} - H \| = \left(\sum_{\substack{m,i \\ (m \in S)}} |\langle \psi_m | H^{ps} - H | \psi_i \rangle|^2 \right)^{1/2} \tag{81}$$

$$= \{ \mathrm{Tr}[P(H^{ps} - H)^2] \}^{1/2}.$$

From a practical point of view, the determination of a pseudo-Hamiltonian by minimizing the distance between H^{ps} and H has the decisive advantage of

keeping simple linear mathematics. However, it has the drawback that there is no guarantee concerning the energies of H^{ps} belonging to $S^{\perp}$. They can enter the desired region of energies or even go below the energies of H^{ps} obtained by simulation in S. To eliminate these spurious unphysical intruder states, one can proceed as follows. First one diagonalizes H^{ps} characterized by an initial choice of parameters. The N_m lowest solutions ψ'_m with energies E'_m define a subspace S', the projector of which is P'. In a second step one minimizes the distance between $P'H^{ps}P'$ and PHP. The reduced distance can be taken either in S or in S':

$$\| H^{ps} - H \|_S = \{ \mathrm{Tr}[P(P'H^{ps}P' - PHP)]^2 \}^{1/2}$$

$$= \left(\sum_{m,n=1}^{N_m} \left| \sum_{p=1}^{N_m} (E'_p S_{mp'} S_{p'n} - E_p \delta_{mp} \delta_{pn}) \right|^2 \right)^{1/2} \tag{82}$$

$$\| H^{ps} - H \|_{S'} = \{ \mathrm{Tr}|P'(P'H^{ps}P' - PHP)|^2 \}^{1/2}$$

$$= \left(\sum_{m,n=1}^{N_m} \left| \sum_{p=1}^{N_m} (E'_p \delta_{mp} \delta_{pn} - E_p S_{m'p} S_{pn'}) \right|^2 \right)^{1/2} \tag{83}$$

where $S_{mp'}$ and $S_{p'n}$ denote the overlaps $\langle \psi_m | \psi'_p \rangle$ and $\langle \psi'_p | \psi_n \rangle$, respectively. Expressions (82) and (83) clearly indicate that their minimization implies that the N_m lowest solutions of H^{ps} (wavefunction and energies) are as close as possible to the N_m solutions of H. The minimization of (82) or (83) provides new parameters for H^{ps} and the above two-step procedure must be repeated until the determination of a fixed parametrization for H^{ps}. The drawback of the method is that it is highly non-linear and that the self-consistent procedure may become very computer-time-consuming for many-body problems.

2. *The Concept of Truncated Hamiltonian*

Up to now it has been considered that the pseudo-Hamiltonian H^{ps} should simulate the exact Hamiltonian H. This means that, at least for a part of the spectrum, the solutions of H^{ps} (energies and wavefunctions) look like those of H. This is not always the best way to proceed since the main purpose of theoretical *ab initio* modelling is to derive pseudo-Hamiltonians that possess for part of the spectrum energies as close as possible to the exact energies and *simplified* truncated wavefunctions belonging to some well characterized predetermined model space. For instance, one may wish to project the physics in the space of all Slater determinants arising from a minimal basis set of atomic orbitals. For that purpose, it may be convenient to introduce some truncated Hamiltonian defined only in a restricted space. Figure 6 gives a schematic illustration of the intermediate role played by such a truncated Hamiltonian, denoted H^{tr}, which appears as a new intermediate step for deriving a pseudo-Hamiltonian from an exact Hamiltonian. H^{tr} is defined in

some significant model space S_0, the projector of which is P_0. Its spectral decomposition can be written as

$$H^{tr} = \sum_{m=1}^{N_m} E_m |\psi_m^0\rangle\langle\psi_m^0| \tag{84}$$

Expression (84) defines a Hermitian Hamiltonian. A possible choice for H^{tr} is obviously the des Cloizeaux effective Hamiltonian or some of its generalizations investigated in Section II.A. With this choice, the E_m of (84) remain exact energies of the original exact Hamiltonian H. But other choices are possible for H^{tr} that also may be characterized by its matrix elements. The best pseudo-Hamiltonian is now obtained by minimizing the distance

$$\| H^{ps} - H^{tr} \| = \{ |\mathrm{Tr}[P_0(H^{ps} - H^{tr})]|^2 \}^{1/2} \tag{85}$$

or equivalently by requiring

$$(H^{ps} - H^{tr} | H^{ps} - H^{tr})_{\text{minimum}} \tag{86}$$

Up to now the conceptual importance of this truncated Hamiltonian does not seem to have been clearly recognized. According to our experience in the field, it is most often a necessary intermediate step for deriving pseudo-operators and pseudo-Hamiltonians from exact Hamiltonians by first principles. This will be clearly indicated by applications in Section IV.

III. APPLICATIONS OF EFFECTIVE HAMILTONIANS

A. Relativity

For heavy atoms, the instantaneous velocities of the electrons near the nuclei cannot be neglected with respect to the velocity of light. These electrons must be described within the Dirac relativistic theory. For the sake of simplicity, let us consider a one-electron system in a central field. The Dirac Hamiltonian, shifted for the energy by c^2, can be written in atomic units (a.u.) as

$$H = (\beta - 1)c^2 + c\boldsymbol{\alpha}\cdot\mathbf{p} + V \tag{87}$$

Here $\boldsymbol{\alpha}$ and β are the four-component matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} \tag{88}$$

where $\boldsymbol{\sigma}$ are the Pauli matrices in their standard representation and I is the 2×2 unit matrix; c is the velocity of light ($c = 137$ in atomic units) and $V = V(r)$ depends only on the distance r between the electron and the nuclei.

Most often we are interested in solutions corresponding to the negatively charged electrons of chemistry and physics, the so-called positive-energy

solutions.[46] For these solutions the first two components ψ_1 and ψ_2 of ψ are large with respect to the small components ψ_3 and ψ_4. Thus it seems obvious that one has to look for two-component formalisms, which were first investigated by Pauli. Foldy and Wouthuysen[47] have shown that, by means of successive unitary transformations, it is possible to expand in a systematic way the Pauli Hamiltonian in powers of $1/c^2$. Unfortunately, this series is highly singular for a Coulomb potential and it results that the standard two-component Pauli Hamiltonian cannot be used for variational calculations.

The purpose of this section is to show how the problem of passing from the four-component Dirac equation to two-component Pauli-like equations can be systematically investigated within the framework of the theory of effective Hamiltonians.[10,11] Beyond the above-mentioned difficulties, we will be able to derive energy-independent two-component effective Hamiltonians that can be used for variational atomic and molecular calculations. To introduce the subject and the notation, let us first consider the simple case of a free electron.

1. Free Electron ($V = 0$)

Hamiltonian (87) reduces to

$$H = (\beta - 1)c^2 + c\boldsymbol{\alpha}\cdot\mathbf{p} \tag{89}$$

Within the energy-dependent Feschbach–Löwdin approach (Section II.A.2) one obtains

$$\Omega_E = P_0 + \frac{1}{1 + E/2c^2}\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}P_0 \tag{90}$$

and

$$H_E^{\text{eff}} = \frac{1}{1 + E/2c^2}\frac{p^2}{2}P_0 \qquad p^2 \equiv -\Delta \tag{91}$$

Within the energy-independent Bloch formalism (Section II.A.3), the reduced wave operator (33) can be written as

$$X = \frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2c}P_0 - X\frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2c}X \tag{92}$$

The exact solution of this equation is[10]

$$X = \frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}\hat{f} \qquad \hat{f} = \frac{2}{1 + (1 + p^2/c^2)^{1/2}} \tag{93}$$

where $\hat{f}$ is a kinetic cut-off operator, which tends towards $2c/p$ for high values of p. From X, the Bloch and des Cloizeaux Hamiltonians can easily be obtained. In the particular case of a free electron, they have the same

expression:

$$H^{\text{eff}}(\text{Bloch}) = H^{\text{eff}}(\text{des Cloizeaux}) = \tfrac{1}{2}p^2\hat{f} \tag{94}$$

Note that by adding the energy c^2 (in a.u.) these effective Hamiltonians can be put in the usual form:

$$H^{\text{eff}} = c^2 + \tfrac{1}{2}p^2\hat{f} = c^2(1 + p^2/c^2)^{1/2} \tag{95}$$

2. *Central-field Potential*

In the presence of V, the Feschbach–Löwdin wave operator becomes

$$\Omega_E = P_0 + \frac{1}{1 + (E - V)/2c^2}\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}P_0 \tag{96}$$

and

$$H_E^{\text{eff}} = \boldsymbol{\sigma}\cdot\mathbf{p}f_E\boldsymbol{\sigma}\cdot\mathbf{p} + V \tag{97}$$

where

$$f_E = \frac{1}{1 + (E - V)/2c^2} \tag{98}$$

is a cut-off function of r which for a Coulomb potential ($V = -Z/r$) tends towards zero with r (Fig. 7).[48,49]

Within the energy-independent Bloch approach, the reduced wave operator becomes

$$X = \frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}P_0 + \frac{1}{2c^2}[V, X] - X\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}X \tag{99}$$

$[V, X]$ is the commutator of V and X. The iterative solution of (99) leads to the perturbation expansion

$$X = \frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}P_0 + \frac{1}{4c^2}[V, \boldsymbol{\alpha}\cdot\mathbf{p}]P_0 - \frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{8c^3}p^2P_0 + \cdots \tag{100}$$

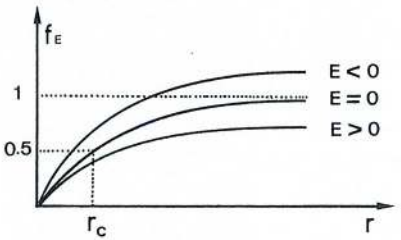


Fig. 7. The cut-off function f_E as a function of the distance r between the electron and the nucleus. For a Coulomb potential, the cut-off radius is $r_c = Z/2c^2$, where Z is the atomic number and c is the velocity of light.

From knowledge of X one can easily derive the Bloch and des Cloizeaux effective operators:

$$H^{\text{eff}}(\text{Bloch}) = -\frac{\Delta}{2} + V - \frac{\Delta^2}{8c^2} - \frac{1}{4c^2}\left(\frac{\mathrm{d}}{\mathrm{d}r}\right)^{\dagger}\frac{\mathrm{d}V}{\mathrm{d}r} + \frac{1}{4c^2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\boldsymbol{\sigma}\cdot\mathbf{L} + \cdots \tag{101}$$

$$H^{\text{eff}}(\text{des Cloizeaux}) = -\frac{\Delta}{2} + V$$

$$-\frac{\Delta^2}{8c^2} \quad +\frac{\Delta V}{8c^2} \quad +\frac{1}{4c^2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\boldsymbol{\sigma}\cdot\mathbf{L} + \cdots \tag{102}$$

mass Darwin spin–orbit

correction

The Hermitian des Cloizeaux effective Hamiltonian is identical to the Pauli Hamiltonian obtained by means of the Foldy–Wouthuysen transformation. It is highly singular for a Coulomb potential, since the Darwin term becomes proportional to the Dirac function $\delta(\mathbf{r})$ and since the spin–orbit term behaves as r^{-3} near the nucleus. Even worse, the series diverge for higher terms in $1/c^4$, which would imply the meaningless product of Dirac functions. Moss *et al.*[50–52] have studied these singularities and searched for methods to avoid these divergences and eliminate the singularities. However, it is easier to notice that the perturbation expansion of X from (99) is incorrect near the nucleus where V becomes infinite and for instantaneous classical velocities of the electron greater than c. To isolate such a strong singularity one has to look for some infinite summation in (99). This can easily be performed if (99) is written in the form

$$X = f\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}P_0 - \frac{f}{2c^2}XV - fX\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2c}X \tag{103}$$

where

$$f = \frac{1}{1 - V/2c^2} \tag{104}$$

For a Coulomb potential the cut-off function f varies from 0 to 1 as illustrated in Fig. 7. The iterative solution of (103) provides regular terms that finally lead to a regular expansion of the Bloch and des Cloizeaux effective Hamiltonians. The first terms are:

$$H^{\text{eff}}(\text{Bloch}) = -\tfrac{1}{2}\Delta_1 + V - \frac{1}{8c^2}\Delta_2\Delta_1 + \frac{1}{4c^2}\Delta_2 V + \cdots \tag{105}$$

$$H^{\text{eff}}(\text{des Cloizeaux}) = -\tfrac{1}{2}\Delta_1 + V - \frac{1}{16c^2}(\Delta_2\Delta_1 + \Delta_1\Delta_2) + \frac{1}{8c^2}(\Delta_2 V + V\Delta_2) + \cdots \tag{106}$$

where

$$\Delta_k = \boldsymbol{\sigma}\cdot\mathbf{p} f^k \boldsymbol{\sigma}\cdot\mathbf{p} \tag{107}$$

These effective Hamiltonians are regular near the nuclei. They provide accurate results for atoms and open the way for relativistic variational two-components calculations in molecules.[53]

B. Research on Nearly Diabatic Potential Energy Surfaces

1. Difficulties of Adiabatic Approaches; Interest in Nearly Diabatic Treatments

It is well known that the solutions of the electronic Hamiltonian H^{el} for a molecule in the Born–Oppenheimer approximation define potential energy curves or surfaces that do not cross when they belong to the same symmetry (except for a few nuclear configurations for which essential or accidental degeneracies may occur). It is also well known that in most cases the molecular wavefunctions keep a well defined dominant character, at least in some regions of the nuclear configuration space. They are for instance valence *or* Rydberg, ionic *or* neutral. When following the *i*th root of the electronic Hamiltonian, the dominant character may change when the nuclear configuration changes. For instance in a diatom, like Na_2 (Fig. 8), the second $2^1\Sigma_u^+$ root[54,55] is essentially 'Rydberg' Na(4s) + Na(3s) at long interatomic distances and it generates a rather flat potential curve. Then at shorter distances, it becomes essentially ionic, dominated by a $Na^+ + Na^-$ $(3s^2)$ character, and the corresponding potential curve is attractive, due to r^{-1} electrostatic interaction. At still shorter interatomic distances the same root changes its physical content to become essentially of Na(3s) + Na(3p) valence-promoted character, and the curve becomes repulsive, defining a long-range minimum near 12 bohr. At still shorter interatomic distances ($r < 10$ bohr), the dominant character changes once more, becoming dominated by a Rydberg character and attractive (as is the Na_2^+ potential curve) (Fig. 8). This *adiabatic* description, in which the potential curves do not cross (no electronic coupling between the adiabatic states), leads to wavefunctions that change their electronic content from one region of the configurational space to another. It is well known[56,57] that one might be tempted to propose an alternative picture where the wavefunctions would keep an invariant content but would of course be electronically coupled. If the derivative $\partial\psi/\partial r$ of the wavefunctions were strictly zero, the representation would be said to be *diabatic*. The dynamic (collisional or vibronic) treatments which follow the calculation of potential energy curves require computation of radial couplings, i.e. $\langle\psi_i|\partial\psi_j/\partial r\rangle$ matrix elements between the adiabatic wavefunctions, and if the function ψ_i changes its character rapidly the derivative is a sharp function of the nuclear coordi-

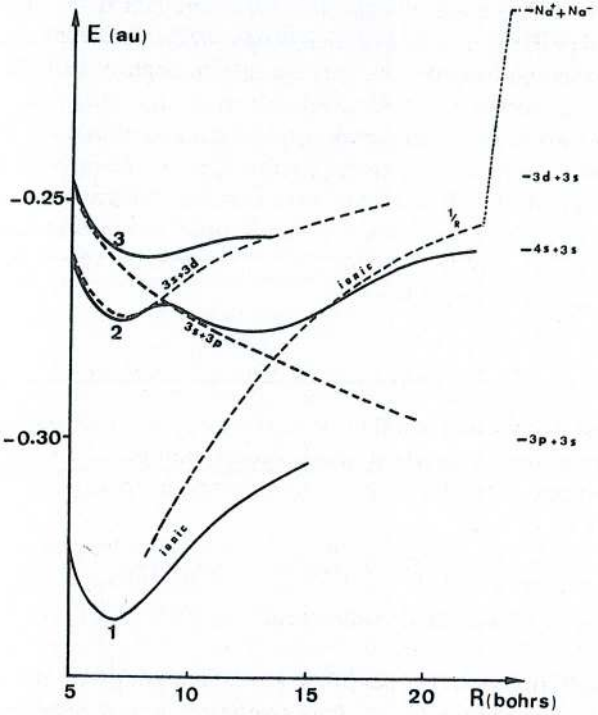


Fig. 8. Illustration of the changes in the content of an adiabatic wavefunction and of a qualitative diabatic reading. Case of the $2\,^2\Sigma_u^+$ state of Na_2.

nates.[58] Owing to this rapid variation, the integration of the matrix element $\langle \psi_i | \partial \psi_i / \partial r \rangle$ requires the calculation of the wavefunctions for a very dense series of nuclear geometries, and it is therefore either very costly or inaccurate.

One has thus in principle a choice between adiabatic and diabatic approaches

Adiabatic	*Diabatic*
Solve $H^{el}\psi = E\psi$	Use diabatic wavefunctions
No electronic coupling	No radial coupling
Radial coupling difficult to calculate	Large and numerous electronic couplings

depending on the privilege given to a preliminary research of the electronic Hamiltonian solutions. The adiabatic approach has the advantage of reducing the dynamic or vibronic problem to a few adiabatic states close in energy, since the radial coupling cannot mix states lying too far apart in energy. The diabatic approach faces two difficulties: (i) It is general impossible[59] to find or

to use strictly diabatic wavefunctions. One is compelled for instance to use valence-bond (VB) determinants which keep a well defined physical character when the nuclear coordinates are varying, and to neglect their derivatives (or to interpolate them). (ii) The electronic wavefunction has in principle to be developed on a very large number of determinants to obtain reliable energies.

Both approaches have then their practical defects. As far as the wavefunction is dominated by a few VB determinants or configurations (a Rydberg configuration crossing a valence repulsive curve, for instance), one may of course restrict the problem to this space and give an approximate elegant diabatic picture of the problem.[57]

2. *Ab Initio Nearly Diabatic Treatments*

There exist two ways to combine the numerical accuracy requirement with the desire of a simple nearly diabatic representation of the problem. One solution consists of performing a unitary transformation on the set of n eigenvectors ψ_k^a of H^{el}:

$$\{\psi_i^d\} = U\{\psi_k^a\} \qquad i,k = 1,2,\ldots,n \tag{108}$$

$$\sum_{i,j} |\langle \psi_i^d | \partial \psi_j^d / \partial r \rangle| = \text{minimum} \tag{109}$$

U being such that the $\langle \psi_i^d | \partial \psi_j^d / \partial r \rangle$ radial couplings of the transformed wavefunctions are minimum.[60] This condition is not very useful from a practical point of view since it requires the knowledge of the radial couplings in the adiabatic basis, which are difficult to calculate. A more practical solution[61] consists of maximizing the overlap of the transformed vectors ψ_k^d with unvariant asymptotic vectors ψ_k^0:

$$\sum_k |\langle \psi_k^d | \psi_k^0 \rangle| = \text{maximum} \tag{110}$$

This procedure gives nearly diabatic vectors; their radial couplings may be either neglected or interpolated, since the ψ_k^d vary slowly with nuclear coordinate changes (see also Ref. 62).

Instead of working in a stable subspace of H^{el} (i.e. in a basis of 10p determinants), one may work in a basis of a rather limited number of configurations, those which play a major role in the adiabatic eigenfunctions of interest, and build an effective electronic Hamiltonian in this model space. For instance, for the curve crossing between the ionic and neutral configuration in NaCl, one may define as a model space the two leading configurations

$$\phi_n = |4s_{Na}^1 3s_{Cl}^2 3p_{Cl}^5| \qquad Na{\cdot}Cl{\cdot} \qquad \text{neutral}$$

$$\phi_i = |3s_{Cl}^2 \text{-} 3p_{Cl}^6 \text{-}| \qquad Na^+Cl^- \qquad \text{ionic}$$

If the treatment was limited to these two determinants with a common set of $3s_{Cl}3p_{Cl}$ atomic orbitals (AO) taken from either the Cl· or Cl^- Hartree–Fock (HF) calculation, the treatment would be quite incorrect and would predict an erroneous curve crossing distance and avoidance. But one may use these two determinants to define a 2×2 model space and apply the theory of effective Hamiltonians, as suggested by Levy[63,64] (with a slightly non-orthodox definition of the effective Hamiltonian). One may use either the Bloch or des Cloizeaux definition of H^{eff} as a 2×2 matrix, the eigenvalues of which are the exact adiabatic eigenvalues

$$\begin{bmatrix} H_{ii}^{\text{eff}} & H_{in}^{\text{eff}} \\ H_{ni}^{\text{eff}} & H_{nn}^{\text{eff}} \end{bmatrix} \Phi_{m,0} = \varepsilon_m \Phi_{m,0} \tag{111}$$

where

$$H^{\text{el}}\psi_m = \varepsilon_m \psi_m$$

$$\Phi_{m,0} = \langle \phi^n | \psi_m \rangle \phi_n + \langle \phi^i | \psi_m \rangle \phi_i \tag{112}$$

The matrix elements of H^{eff} may be obtained from a former large CI diagonalization, by perturbative expansions, or by iterative techniques.

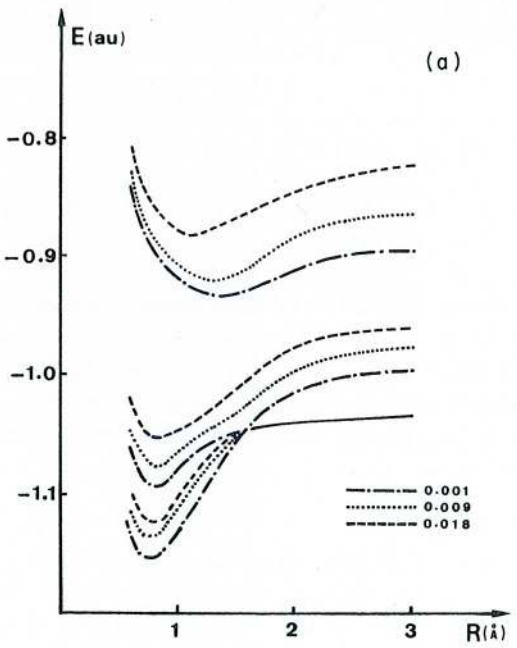
Spiegelmann and Malrieu have proposed improved versions of this procedure,[65] where the model space is spanned by several multi-configurational zeroth-order descriptions of the various diabatic eigenfunctions. This proposal, which fits very well the architecture of the CIPSI algorithm,[66,67] has received applications on Ar_2^* excited states, NaCl curve crossing,[65] $HeNe^{2+}$[64] and the $Cs^*(7p) + H_2(X^1\Sigma_g^+) \rightarrow CsH(X^1\Sigma_g^+) + H$ reactive collision.[68]

Other refinements, combining unitary transformation theory, have been proposed by Persico *et al.*[61] and now seem to be the most rational and efficient procedure to convert the large CI calculations (keeping their energetic reliability) into a simple nearly diabatic picture through a small-sized Hamiltonian. The diagonal (and off-diagonal) terms of this effective Hamiltonian have regular behaviour, since they reflect the variation of the energy of (and coupling between) physically nearly invariant wavefunctions. They may be interpolated easily without loss of accuracy. This solves two types of problems: (i) the calculation of the radial couplings for vibronic problems becomes easy, and (ii) the quantum semiclassical or classical calculations of the dynamical cross-sections requires the knowledge of the energy at a very large number of nuclear configurations; the use of adiabatic potential surfaces usually requires difficult analytic fittings.[69] The analytic fitting of well behaved diabatic potential surfaces and electronic couplings is much easier. One must simply diagonalize a small interpolated effective Hamiltonian when energies are needed in trajectory calculations; this is the philosophy of the use of the DIM method[70] in dynamical calculations, and the *ab initio* nearly diabatic

effective Hamiltonian approach introduces three- (or more) body effects, and ensures a much better reliability of the energies while keeping the same advantage in the dynamics calculations.

3. *A Special Application to Research on Resonant States in e^-–Molecule Collisions*

As a special application of the diabatization techniques of *ab initio* MO-CI calculations, one should mention the research on resonant states in electron–molecule collisions.[71,72] The problem concerns the existence of a discrete (usually valence) state of the molecular anion, embedded in a continuum of diffuse states. For a molecule like H_2, the electronic Hamiltonian of H_2^- has a $^2\Sigma_u^+$ bound state at large interatomic distance (since H^- is stable), while it has no bound state for interatomic distances shorter than 1.4 Å. Collisional properties, however, suggest the existence of a broad resonance of $^2\Sigma_u^+$ character, which may be seen to be due to the coupling of a discrete state of essentially $\sigma_g^2\sigma_u$ valence character with a continuum of diffuse states associated with the $^1\Sigma_g^+$ (σ_g^2) ground state of the molecule, the outer electron being unbound. This problem may be treated in various modes, but it appears as a challenge to quantum chemists, whose finite basis sets seem to forbid the examination of such a problem. Nevertheless some approximate methods have been proposed (known as 'stabilization techniques'[73–76]) to find the



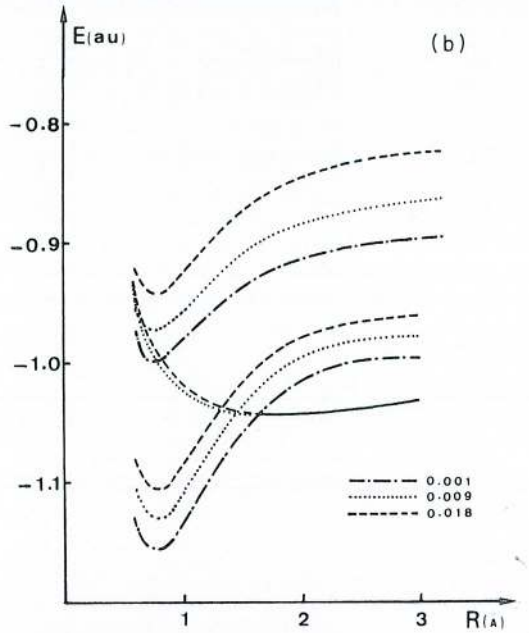


Fig. 9. (a) Adiabatic potential curves of the H_2^- problem in various finite basis set CI calculations.[71] (The numbers refer to the exponent of a diffuse p AO in the centre of the molecule). The full curve refers to the bound-state region. (b) Diabatization of the preceding potential curves;[71] (same comments as in Fig. 8a).

position of the so-called discrete state; for weak couplings between the resonant state and the continuum, the method simply consists in a qualitative diabatic reading of the resonant state potential curve through the avoided crossings with potential curves which are basis set dependent. For strong couplings (broad resonances) some constraints must be added. It may be noticed that finite basis set MO-CI calculations give a sampling of the continuum states through wavefunctions of the type $\phi(X(^1\Sigma_g^+)) \times$ d where d is a diffuse MO. The more diffuse is the d MO, the closer the energy of this unbound state to that of the neutral ground state; the coupling between the hypothetical discrete state, the potential curve of which should be repulsive, and the sampling of diffuse states (with potential curves parallel to the ground-state potential curve) should result in a series of curve crossings, according to Figs. 19a and b.

The usual MO-CI calculations provide adiabatic potential curves. In some cases of weak coupling between the discrete and diffuse states, it has been possible to recognize the place of the discrete potential curve under the net of adiabatic potential curves calculated from various basis sets (see for instance

Ref. 75). This recognition is impossible when the electronic coupling between the discrete and diffuse states is too large (broad resonances). In that case the above-mentioned diabatization procedure may be applied, as suggested by Komiha *et al.*,[71] furnishing a description corresponding to Fig. 8b. The problem is presented as a finite effective Hamiltonian; the model space is spanned by (a) a determinant derived from the asymptotic $H + H^-$ limit, which corresponds to the discrete state, and (b) determinant products of the neutral ground-state wavefunction by a diffuse MO, which have large components in the diffuse states. The eigenvalues of this effective Hamiltonian reproduce the exact adiabatic energies and there is no loss of information regarding the energies. The diagonal matrix element relative to the discrete state, i.e. the potential curve of the diabatic discrete state, fits asymptotically into the bound state in the long-distance region, and presents a well defined and specific shape, *almost independent of the chosen basis set*, for short interatomic distances. In contrast, the positions of the diabatic state potential curves relative to the diffuse states strongly depend on the basis set, but they are always parallel to the neutral ground-state potential curve. The amplitude of the diffuse–discrete electronic coupling depends strongly on interatomic distance. Approximate expressions for the definition of the resonance position and width have been proposed following the basic ideas of Fano,[77] and they appear to give stable results with respect to the choice of the basis set.

C. Reduction of the Number of Particles and/or of the Atomic-orbital Basis Set Through Effective Hamiltonian Approaches: Construction of Valence-only Effective Hamiltonians

1. Preliminary Remarks

The present section essentially discusses the attempts to build effective valence-only Hamiltonians spanned by a valence minimal basis set, which has been the subject of several tens of papers by Freed *et al.* (reviewed in Ref. 78; see also Westhaus[79] and Mukherjee[80]). One should notice first that the purpose of such attempts is two-fold: elimination of the core electrons from the explicit treatment; and reduction of the basis set for the treatment of the valence states of the molecule to a minimal valence basis set. The effective Hamiltonian should reproduce the energetic results of a calculation including the core electrons, their exclusion, polarization and correlation effects, and performed in a large basis set (for both the concentrated core distribution and the more diffuse valence cloud).

From a basic point of view, the two purposes are different and should be distinguished; one may be tempted to eliminate the core electrons while keeping a non-minimal valence basis set, as occurs in pseudopotential techniques, on the one hand, while on the other hand, one may try to treat a coreless problem such as a cluster of hydrogen atoms in a minimal basis set, or

treat both the core and the valence shells in a minimal basis set. The present section will try to analyse the two purposes independently, in order to simplify the discussion.

As a second important point, one should note that the reduction of the number of electrons or of the basis set, which may be performed through the effective Hamiltonian theory on the atom or on a diatom, is of little interest if it is not used in the treatment of *larger* systems. The reduction of the information on a diatomic problem is not an interesting problem *per se*, it is only worth while if it results in *transferability* of effective interactions from small to large systems. The present section will always discuss the effective Hamiltonian reliability from this point of view, which initiated the work of Freed when he realized that effective Hamiltonian theory might give a strong ground and a practical *ab initio* derivation to the very cheap and quite inelegant (since resting on trial and error in the determination of the parameters) semi-empirical Hamiltonians of quantum chemistry. We shall not discuss the practical successes of the attempts of transfer, which are quite limited, but its theoretical legitimacy, from the basic content of the model spaces.

The present section will be organized as follows. It first analyses briefly the effect of the core electrons on the valence energies, and which are the main impacts of enlargement of the valence basis set for the molecular calculation. This will be done on an elementary problem, an alkali diatom, and the analysis will be performed through an appropriate orthogonal valence-bond (OVB) approach. The strategy followed by Freed and coworkers will then be briefly reported. It rests on a low-order degenerate perturbative expansion which faces difficult problems, some of them being mentioned there. The next subsections move to the basic definition of H^{eff}. In a following subsection, the chances of eliminating the core electrons are briefly discussed, in order to compare with the pseudopotential techniques discussed elsewhere. The last subsection discusses a few difficulties for deriving a minimal basis set effective Hamiltonian, namely intruder state problems, especially at large interatomic distances and the occurrence of intrinsically new valence situations in a polyatomic molecules valence problem, which cannot be derived from diatomic interactions.

This section concludes that, despite its advantages, the attempts to define complete valence effective Hamiltonians will probably face tremendous problems, owing to the large heterogeneity of the valence spectrum, which involves low-lying neutral states and up to multiply ionic states embedded in a far continuum (autoionizing states).

2. *Role of Core Electrons and of Basis Set Extension. Analysed for an Alkali Diatom Problem*

The simplest typical problem concerns the alkali diatom (Li_2) or the ethylene molecule. The active electrons are the two valence 2s electrons or the

two π electrons, and the effective space is generated by two 2s or two $2p_z$ AOs a and b supposed to be properly orthogonalized (*vide infra*). The core electrons represent either the 1s pairs or the σ frame. For the sake of simplicity, we reduce the core to one electron pair, for instance the localized C–C bond pair, in one σ_g MO. The model space is spanned by four determinants, two of them being neutral, two of them being ionic in the sense of VB theory

$$P_0 = \sum_{i=1}^{n} |\phi_i\rangle\langle\phi_i|$$

$$\left.\begin{aligned}\phi_1 &= |\sigma\bar{\sigma}a\bar{b}| \\ \phi_2 &= |\sigma\bar{\sigma}b\bar{a}|\end{aligned}\right\} \mathrm{A\cdot B\cdot} \quad \text{neutral}$$

$$\left.\begin{aligned}\phi_3 &= |\sigma\bar{\sigma}a\bar{a}| \\ \phi_4 &= |\sigma\bar{\sigma}b\bar{b}|\end{aligned}\right\} \begin{matrix}\mathrm{A^-B^+} \\ \mathrm{A^+B^-}\end{matrix} \quad \text{ionic} \qquad (113)$$

The first-order Hamiltonian keeps the form

$$\begin{array}{cccc} \phi_1 & \phi_2 & \phi_3 & \phi_4 \\ \hline 0 & K_{ab} & F_{ab} & F_{ab} \\ & 0 & F_{ab} & F_{ab} \\ & & \Delta E & K_{ab} \\ & & & \Delta E \end{array} \qquad (114)$$

where K_{ab} is an interatomic exchange integral, F_{ab} is a hopping integral and ΔE, the transition energy from the neutral to the ionic determinants, is positive. If these four determinants define the model space, the corresponding effective Hamiltonian will keep the same structure, imposed by symmetry. In Hermitian formalisms the outer space will change the matrix into

$$\begin{array}{cccc} -\delta E & K_{ab}+\delta K & F_{ab}+\delta F & F_{ab}+\delta F \\ & -\delta E & F_{ab}+\delta F & F_{ab}+\delta F \\ & & \Delta E-\delta E' & K_{ab}+\delta K' \\ & & & \Delta E-\delta E' \end{array} \qquad (115)$$

and the question under analysis is the understanding of the main differences between this effective OVB matrix and the first-order one.

This matrix may be factorized by spin and space symmetries into a one-dimensional triplet antisymmetric, a one-dimensional singlet antisymmetric and a two-dimensional singlet symmetric subspaces

$$^3\mathrm{A} = (\phi_1 - \phi_2)/\sqrt{2}$$
$$^1\mathrm{A} = (\phi_3 - \phi_4)/\sqrt{2}$$
$$^1\mathrm{S}_1 = (\phi_1 + \phi_2)/\sqrt{2}$$
$$^1\mathrm{S}_2 = (\phi_3 + \phi_4)/\sqrt{2}$$

The outer space will involve two types of determinants: (i) those which keep the frozen σ core, and (ii) those involving excitations from the σ core. The former represent the effect of an extension of the valence basis set, and their effect may be analysed first.

We may assume first that the a and b orbitals have been determined self-consistently for the lowest triplet state ^{3}A which is neutral in character since the $S_z = 1$ solution may be written unambiguously by a localization of the symmetry-adapted singly occupied MOs, into a localized picture[81]

$$^3\mathrm{A} = |\sigma\bar{\sigma}ab| \tag{116}$$

and obtained from a preliminary restricted Hartree–Fock (RHF) calculation. One should notice that the distortion of these two localized MOs a and b with respect to the free-atom RHF AOs $\tilde{a}'$ and $\tilde{b}'$ is very important. It involves, besides orthogonalization tails, contractions and distortions in the molecular field and significant hybridizations which minimize the electronic repulsion, avoiding for instance the neighbouring core:

$$a = \tilde{a}' + \sum_{\substack{p\in A \\ p\neq\tilde{a}}} C_{ap}p + \sum_{q\in B} C_{aq}q$$

These preliminary distortions are of major energetic importance.

Then one may introduce orthogonal atomic orbitals a_i' and b_i', which are excited atomic orbitals of A and B orthogonalized to a and b, and one will generate single and double excitations towards these virtual MOs from either neutral (ϕ_1, ϕ_2) or ionic (ϕ_3, ϕ_4) valence determinants.

Single excitations from ϕ_1 or ϕ_2 will generate

$$\langle\sigma\bar{\sigma}a_i'\bar{b}|H|\phi_1\rangle = \langle a_i'| - K_b|a\rangle = (a_i'b, ab)$$

i.e. rather small corrections (due to the weakness of the interatomic distributions). K_b is the exchange operator associated with orbital b. Double excitations from ϕ_1 or ϕ_2 will generate

$$\langle\sigma\bar{\sigma}a_i'\bar{b}_i'|H|\phi_1\rangle = \langle a_i'b_i'|ab\rangle = (a\acute{a}_i, bb_i')$$

i.e. stabilizing interatomic dispersion forces, of moderate amplitude. Single excitations from ϕ_3 or ϕ_4 will lead to much larger corrections since the matrix element represents

$$\langle\sigma\bar{\sigma}a_i'\bar{a}|H|\phi_3\rangle = \langle a_i'|J_a - J_b|a\rangle$$

i.e. the coupling of the $(a_i'a)$ dipolar distribution with the valence dipolar field of the A^-B^+ distribution, where J_a and J_b are the coulomb operators associated with orbitals a and b respectively. This represents both an atomic reorganization of the A^- electron pair (which tends to be more diffuse) and its molecular distortion towards the B^+ centre. Double excitations from ϕ_3

or ϕ_4) will lead to

$$\langle \sigma\bar{\sigma}a_i'\bar{a}_j'|H|\phi_3\rangle = \langle a_i'a_j'|aa\rangle = (aa_i', aa_j')$$

corrections correlating the electron pair of the negative ion A^-, either radially if a_i' and a_j' have the same l value l_a, or angularly if a_i' and a_j' have a value of $l = l_a \pm 1$. Double excitations from the ionic valence components therefore introduce the radial and angular correlation of the monocentric electron pair.

The conclusion is thus that the extension of the basis set with respect to the minimal atomic basis set is important (i) to distort the AOs in order to minimize the interatomic repulsion in the *neutral* forms, and (ii) to lower the energies of the *ionic* components of the VB wavefunction by important instantaneous repolarization and correlation effects.[82-84]

If the atoms bear more than one electron, for instance for a carbon atom, the VB wavefunction of a C-containing molecule will introduce some components where the C atom is neutral, in several possible s^2p^2, sp^3, p^4 valence states (the latter being hybridized), and other components of C^+, C^-, C^{2+}, C^{2-}, ... singly or multiply ionic character. The use of large basis sets in CI calculations essentially results in lowering of the effective energies of the various excited neutral, ground and excited ionic valence states appearing in the full valence CI wavefunction.

The influence of core excitations may be studied according to a similar analysis. One may first consider $\sigma \rightarrow \sigma^*$ single excitations. The effect on the neutral determinants ϕ_1, ϕ_2

$$\langle \phi_1|H|a_{\sigma^*}^+ a_\sigma \phi_1\rangle = \langle \sigma| - K_b|\sigma^*\rangle$$

is weak, due to Brillouin's theorem. In contrast, single excitations acting on the ionic determinants ϕ_3, ϕ_4, lead to a very important coupling

$$\langle \phi_3|H|a_{\sigma^*}^+ a_\sigma \phi_3\rangle = \langle \sigma| - J_a + J_b|\sigma^*\rangle$$

which represents the coupling between the $\sigma\sigma^*$ transition dipole and the A^-B^+ valence dipole.[85] The corresponding correction represents the repolarization of the σ core under the instantaneous valence field of the ionic valence determinants. This correction will be a major molecular correction.

Double excitations involving two core electrons introduce core correlation effects, almost independent of the valence electron distribution; they have a pure translational effect on the energies.

Double excitations involving both one core and one valence electron $a_{\sigma^*}^+ a_{a_i}^+ a_a a_\sigma$ lead to $(\sigma\sigma^*, aa_i')$ matrix elements when they act on either the neutral or the ionic determinants. Their effect is essentially translational on the valence states. They stabilize the Rydberg states much less and become zero in the positive ion. They thus have an important spectroscopic effect,[86-90] but

they are not crucial for the energy differences between *valence* states of the neutral molecule.

One should therefore remember that *the main effect of the core appears from single excitations on the valence ionic VB components.*

One thus sees that the core electrons will essentially act as a polarizable system, sensitive to the electric field instantaneously created by the valence electrons. This field is especially large in ionic VB components and the core–valence interaction should essentially result in a differential stabilization of the valence VB ionic structures with respect to the valence-only approach.

Therefore, both valence basis set enlargement and core correlation effects might be seen as going essentially through a coupling with the *ionic* components of the valence wavefunction. One may thus imagine immediately that their effect will be some specific energy lowering of these ionic VB component energies, with respect to those that one would predict from a frozen-core and/or from a minimal basis set calculation. In Eq. (115) the larger corrections will be $\delta E'$. In an effective Hamiltonian calculation the effect of these corrections will essentially be a *dressing of the ionic VB components*, i.e. a lowering of the self-repulsion, as well known in π-electron theories.

3. *Simultaneous Reduction of the Number of Particles and Basis Set; the Valence Effective Hamiltonians of K. Freed*

In a large series of papers, Freed and coworkers have tried to define valence-only minimal basis set effective Hamiltonians. This idea was first applied to the π system of conjugated hydrocarbons, eliminating the explicit treatment of the σ core and attempting to find rigorous foundations[91–94] for the π semi-empirical Hamiltonians of the Pariser–Parr–Pople family,[95,96] or to obtain non-empirical derivations of these simplified Hamiltonians. The CNDO valence-only Hamiltonians[97] excluded the $1s^2$ core electrons of the atoms and belonged to the same category. The same idea therefore received numerous other applications to atoms[98] (including transition metals[99,100]), hydrides.[101,102] alkali diatoms,[103,104] diatoms with more than two valence electrons (O_2),[105–107] etc.

The method[108–110] is frequently referred to as the partitioning (Feshbach–Löwdin) technique (see Section II.2). The model space is the valence complete active space, i.e. the whole set of determinants involving the same (unspecified) frozen core and all possible electronic distributions in the valence orbitals. This space is, of course, very large and spread on a huge range of energies. For O_2, for instance, it involves $O(2p^6) + O(2p^6)$ configurations, which are unbound. It also involves, for instance, $O^{2-}(2s^2p^6) + O^{2+}(2p^4)$ situations, which also generate unbound states at all distances. If the effective Hamiltonian was that produced by the partitioning technique, it would be energy-dependent. In other words, one would have a different valence effective

Hamiltonian for each state. The effective integrals would then be very difficult to transfer to larger problems. The first papers on π electron effective Hamiltonians were actually presented as energy-dependent.

In most papers, Freed *et al.*[108,110] (i) develop the energy denominator of Eq. (9) in a power expansion, thus going back to a Rayleigh–Schrödinger version of the quasi-degenerate perturbation theory (QDPT); (ii) use a monoelectronic definition of $H_0 = \sum_i \varepsilon_i a_i^+ a_i$ (Moller–Plesset definition of the unperturbed Hamiltonian); (iii) introduce a full degeneracy of the valence space, which, while this complete degeneracy results from the choice of H_0 in the case of a single band, further requires giving equal energies to *s* and p AOs in systems involving both s and p orbitals; (iv) define a set of rationally orthogonalized AOs by a proper combination of Schmidt and $S^{-1/2}$ transformations. Alternative definitions of localized equivalent orbitals may be obtained from the valence MOs of the upper multiplet. The QDPT expansion is performed in a basis of OVB determinants.

One should notice first that, from the very theory, the effective Hamiltonian of an *n*-active-electron problem spanned in a basis of *N* determinants is a series of *n-electron operators*

$$H^{\text{eff}} = \sum_{I,J=1}^{N} |\phi_I\rangle\langle\phi_I|H^{\text{eff}}|\phi_J\rangle\langle\phi_J| \tag{117}$$

which are quite difficult to handle if one wants to transfer them into a larger problem. Freed *et al.*[108–110] succeed in expressing the effective Hamiltonian in terms of one-, two-, three-,... particle operators. This is always possible in principle but quite arbitrary. If ϕ_I and ϕ_J differ by two spin orbitals only

$$\phi_J = a_j^+ a_l^+ a_k a_i \phi_I \tag{118}$$

one may be tempted to define the effective bielectronic integral as

$$(ij, kl)^{\text{eff}} = \langle\phi_I|H^{\text{eff}}|\phi_J\rangle$$

but if one considers another couple of determinants, also differing by the same spin orbitals

$$\phi_L = a_j^+ a_l^+ a_k a_i \phi_K \tag{119}$$

the effective interaction has no reason to be the same

$$\langle\phi\ |H^{\text{eff}}|\phi\ \rangle \neq \langle\phi_J|H^{\text{eff}}|\phi_I\rangle \tag{120}$$

since they include high-order processes which are different. If

$$\phi_K = a_m^+ a_n \phi_I \tag{121}$$

one may be tempted to write

$$\langle\phi_K|H^{\text{eff}}|\phi_L\rangle = (ij, kl)^{\text{eff}} + \delta_{ijkl,mn} \tag{122}$$

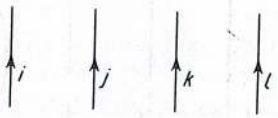
$\delta_{ijkl,mn}$ representing an increment of the (ij, kl) effective interaction when MO *n* is empty and the MO *m* is occupied.

In terms of operators this may be written as a six-body operator

$$\delta_{ijkl,mn} a_j^+ a_l^+ a_k a_i a_n a_n^+ a_m^+ a_m$$

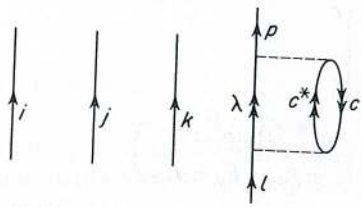
This procedure may be generalized and is well defined, but it depends on the order of appearance of the ϕ_I. If one of the ϕ_I played a special role, as the Hartree–Fock (HF) determinant, it might be taken as the vacuum state, and a hierarchy of singly, doubly,... excited determinants might be defined, but since one is looking for local (transferable) interactions involving orthogonal AOs, all VB determinants play the same role and any ordering would be arbitrary.

Freed *et al.*[108–110] therefore do not follow this way. They expand the effective Hamiltonian to second order, and since all the determinants of the model space are kept degenerate, the second-order corrections only introduce one-, two- and three- particle operators which only depend on the index of the connected propagation lines in the diagram. If one defines the reference description of the core as the vacuum, the model space states are defined by a certain number of upwards propagation lines, equal to the number of valence electrons. For a four-electron problem, the state ϕ_I is defined by the four indices



defining $\phi_I = a_i^+ a_j^+ a_k^+ a_l^+ \phi_C$.

Then a one-body operator may change ϕ_I into $\phi_J = a_p^+ a_l \phi_I$. A second-order correction may be viewed as



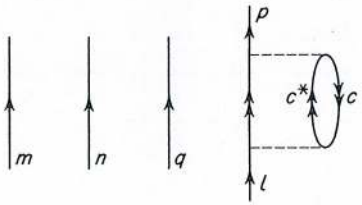
$$= \frac{(cc^*, \lambda l)(\lambda p, cc^*)}{E_c + E_l - E_\lambda - E_{c^*}} \qquad (123)$$

where the double arrows symbolize MOs which do not belong to the active space. The downward

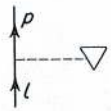
line necessarily concerns a core MO while

and

belong to the virtual space. Now it becomes clear from hypothesis (iii) that the process



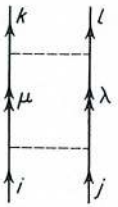
will result in an equal correction and one may say that



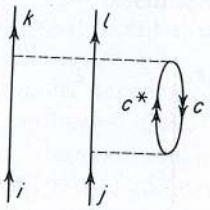
$$\left(\sum_{c} \sum_{c^*} \sum_{\lambda} \frac{(cc^*, \lambda l)(\lambda p, cc^*)}{E_c + E_0 - E_\lambda - E_{c^*}} \right) \tag{124}$$

is the amplitude of an effective second-order correction to the first-order interaction through the core Fock operator.

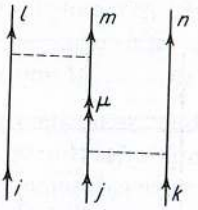
Typical two-body operators are



or



the second diagram involving a core excitation. The three-body terms are of the type

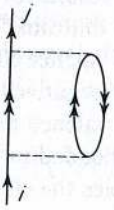


and may change there valence orbitals, but only involve one outer orbital.

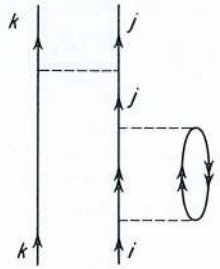
One should notice, however, that the third-order corrections will destroy this apparent simplicity. The third-order corrections are given from Eq. (43) by

$$\langle \phi_I | H^{(3)} | \phi_J \rangle = \sum_{\alpha,\beta \notin S} \frac{\langle \phi_I | V | \alpha \rangle \langle \alpha | V | \beta \rangle \langle \beta | V | \phi_J \rangle}{(E_J - E_\alpha)(E_J - E_\beta)} - \sum_{\alpha \notin S} \sum_{L \in S} \frac{\langle \phi_I | V | \alpha \rangle \langle \alpha | V | \phi_L \rangle \langle \phi_L | V | \phi_J \rangle}{(E_J - E_\alpha)^2} \tag{125}$$

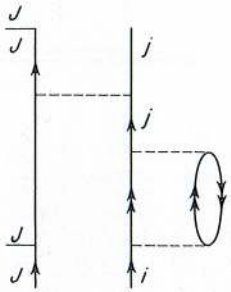
and since the model space involves some valence states of very high energy (for instance, highly hybridized VB structures, or multiply ionic components), some of the diagonal terms of the perturbation operator are actually *huge*. The second summation in Eq. (125) will involve some tremendous terms, which will make the perturbation expansion quite unreliable and will destroy the apparent simplicity of the above-mentioned one-, two-, and three-body operators. For instance the same one-body operator



will be associated with contributions involving other valence MOs, which may have completely different amplitudes:



involves J_{jk} while



involves J_{jj}, which may be much larger. (These diagrams should be folded to enter the canonical diagrammatic QDPT expansion.)

The trick of introducing full degeneracy of the model space is only efficient at the second order, and the transformation of an effective Hamiltonian into one-, two-, three-,... body operators is questionable since from their very definition the effective Hamiltonians are actually N-body operators.

In practice, several questions arise:

1. When one uses a low-order perturbation expansion, resting on a very crude H_0 definition, are the lowest valence potential curves equally correct? The large series of papers by Freed and coworkers devoted to diatoms[101,102,105] actually seem to support a positive answer.
2. Is the transferability to positive and negative (di)atomic ions ensured, when the extraction has been done from neutral (di)atoms? A large series of papers have given satisfactory results for the positive ions of atoms[98] (even when multi-ionized) and of diatoms.[101,106] For negative ions Freed *et al.*[107] claimed that the use of valence effective interactions might solve the difficult resonance problem for negative ions, since it would directly give the potential curves of a dressed valence negative ion, which is supposed to generate the discrete state embedded in the continuum. Again, one should say that from the very principles the effective Hamiltonians for X_2^+ or X_2^-

are completely different from that of X_2. If X = Li for instance the effective Hamiltonian for Li_2^+ cannot in principle be reduced to the one-particle effective operator of Li_2. The most recent attempts to calculate Li_2^+ from Li_2 have actually failed.[103,104]

3. Is the transferability to larger molecules ensured? The derivation of effective interactions from a diatomic problem is useless except for transferability to larger systems. An approach of this main goal has not been even attempted, except for the π systems of conjugated hydrocarbons. In that precise case[94] an effective Hamiltonian has been proposed for butadiene, and keeping the nearest-neighbour interactions from a similar calculation on ethylene, it was possible to estimate long-distance one- and two-body interactions and many-body terms. The results were very discouraging since the one-electron 1–4 hopping integral between the terminal atoms appeared to be as large as -1.6 eV, i.e. of the same order of magnitude as the hopping integral between adjacent atoms ($\beta_{12} = -4.0$ eV).

In view of these practical difficulties, and in order to separate the convergence problems of the perturbative approach from basic problems inherent to the effective Hamiltonians themselves, we would like to reanalyse the core–electron elimination and the reduction of the basis set in basic terms, i.e. referring to the definitions of the exact effective Hamiltonians.

4. Reduction of the Number of Particles

Let us define ϕ_c as an HF or internally correlated description of the core shell of an atom (or a molecule). Then one may choose as a valence model space the set of functions which are antisymmetrized products of ϕ_c by a valence function ϕ_I, in which the n_v valence electrons occupy valence, or Rydberg, or arbitrary orbitals orthogonal to the core orbitals (and not involved in its description)

$$P_0 = \sum_{I \in S} |\phi_c \cdot \phi_I\rangle\langle\phi_c \cdot \phi_I| \tag{126}$$

For the lithium atom, for instance, ϕ_c may be a $1s^2$ product or a linear combination

$$\phi_c = \alpha(1s^2) + \beta(1s'^2) + \gamma(p^2)$$

including the largest part of the radial and angular correlation of the $1s^2$ pair. ϕ_I may include a set of n valence plus diffuse plus oscillating AOs, orthogonal to the core AOs. Then the target subspace, of dimension n, has to be defined. If one defines it as the n lowest roots of the Li problem treated in the same basis set

$$P = \sum_{k=1}^{n} |\psi_k\rangle E_k \langle\psi_k| \tag{127}$$

with

$$H_P|\psi_k\rangle = E_k|\psi_k\rangle \tag{128}$$

H_P being the exact Hamiltonian restricted to the finite AO basis set, one should note two difficulties: (i) If the basis set involves spatially concentrated (oscillating) AOs, some of the roots may be unbound, i.e. embedded in the continuum; they are then strongly dependent on basis set. (ii) Some core excited solutions close, for instance, to $|1s2sns\rangle$ may be lower in energy than some roots keeping a frozen core ($(1s^2ks)$ where ks would be a very concentrated and oscillating AO). This will result in an intruder state problem.

To avoid the arbitrariness noticed in (i), one may introduce a spectroscopic basis set of AOs spanning only the valence and lowest Rydberg states of the atoms. But it is known that the molecular construction implies some orbital contraction, which can hardly be mimicked from spectroscopic AOs. It is also very important when an atom A approaches an atom B that the basis set of the atom B involves same oscillating spatially contracted functions which are used by the outer electron orbitals of A to minimize their repulsion with the electrons of B. It seems almost compulsory for a correct molecular treatment that the atomic information concerns the energy of unbound spatially concentrated atomic distributions. Then the occurrence of the second problem (i.e. the occurrence of core excited intruder states) is not excluded.

The problem is worse when one considers atoms involving several valence electrons. If one wants to obtain the information relative to a double-zeta valence basis set of the C atom, it will be necessary, in principle, to find states of the type $1s^22p^4$ and also $1s^23p^4$; if 2p and 3p are the RHF AOs in the basis set, the latter ($1s^23p^4$) determinant will certainly be higher in energy than core excited states of the type ($1s2s^22p^3$), which will act as intruder states. The definition of the target space will then be quite difficult, since for some basis sets it will be difficult to discriminate between the eigenstates of the problems which keep a frozen core from those which are core excited.

Once the model and target spaces have been chosen, the atomic effective Hamiltonian is defined and its use in molecular calculations may be examined. For the Li atom, for instance,

$$H_A^{\text{eff}} = \sum_{k=1}^{n} |1s^2k\rangle E_k \langle 1s^2k| \tag{129}$$

H_A^{eff} is purely monoelectronic and monocentric. If one goes to Li_2 one may first assume a purely monoelectronic form of the Hamiltonian

$$H_{AB}^{\text{eff}} = H_A^{\text{eff}} + H_B^{\text{eff}} \tag{130}$$

while the basis set will involve $2n$ AOs on A and on B. Then the effective Hamiltonian will reduce to a valence Hückel-type problem

$$(H^{\text{eff}} - ES)C = 0$$

where for instance

$$\langle 2s_A|H^{eff}|2s_a\rangle = E_{2s} + \sum_{k_b}\langle 2s_A|k_B\rangle^2 E_k$$
$$\langle 2s_A|H^{eff}|2s_b\rangle = 2E_{2s}\langle 2s_a|2s_b\rangle$$

It is clear that such a Hamiltonian can only rationalize a Hückel-type Hamiltonian (eventually in a non-minimal basis set) and that it essentially leads to a pure Mulliken-type approximation for the bicentric integrals (which play the key role in the construction of the bond through electron delocalization). It is known that such approximations usually fail; an empirical k parameter is used in the proportionality of the hopping integrals to the overlap and atomic energies (Wolfsberg–Helmholtz approximation).

An alternative strategy consists of considering that

$$E_k = \langle 1s^2k|T - Z_A/r_A + v_A|1s^2k\rangle \tag{131}$$

i.e. that the effect of the core electrons goes through a monocentric correction to the integrals of the (kinetic + nuclear attraction) operator

$$v_A = \sum_k (E_k - \langle 1s^2k|T - Z_A/r_A|1s^2k\rangle)|1s^2k\rangle\langle 1s^2k|$$

The molecular calculation of Li_2 will then be performed through a two-electron Hamiltonian

$$H = T - \frac{Z_A Z_B}{r_A - r_B} + \frac{1}{r_{12}} + v_A + v_B \tag{132}$$

and developed in the basis of determinants $|1s_A^2 1s_B^2 kl\rangle$. The correction operator v_A, which may be considered as a core-potential correction written in a non-local finite expansion, will act on the atomic orbitals centred on atoms A and B.

This procedure offers in principle an alternative to the pseudopotential approaches for the treatment of electron cores. It faces two problems: (i) The non-local expansion of v_A is quite arbitrary. (ii) The process is difficult to generalize to atoms having several valence electrons. For boron atoms, for instance, the effective Hamiltonian should be written

$$\begin{aligned} H^{eff} = {} & |1s^2 2s^2 2p\rangle\langle 1s^2 2s^2 2p|E(^2P) \\ & + |(^4D)1s^2 2s 2p^2\rangle\langle (^4D)1s^2 2s 2p^2|E(^4D) \\ & + |(^2S)1s^2 2s 2p^2\rangle\langle (^2S)1s^2 2s 2p^2|E(^2S) + \cdots \end{aligned} \tag{133}$$

i.e. it is intrinsically trielectronic, without any rigorous reduction to a monoelectronic operator. Attempts along this way have never been practised, and should be performed carefully. The fact that multi-electronic operators are required does not condemn this approach, since these multi-electronic

operators should receive a monocentric expansion and would only generate the calculation of overlap integrals in molecular calculations.

To summarize this section one should say that an effective Hamiltonian treatment of the core electron effect faces a contradiction between the necessity to use extended valence basis sets for the extraction and the risk of appearance of core excited intruder states. One should also recognize that this approach leads to p-electron operators for atoms involving p valence electrons and seems much more difficult to handle than the monoelectronic core pseudopotentials extracted by simulation techniques and discussed in Section IV of the present contribution. As a counterpart one should mention that this core effective Hamiltonian would be much superior, since it would include for instance the core–valence correlation effects which play such an important role in alkali- or alkaline-earth-containing molecules.

5. *Reduction to Minimal Basis Sets*

The problem consists of defining a valence minimal basis set effective Hamiltonian which would reproduce the valence part of the *exact* molecular spectrum. As already mentioned the problem might concern atoms involving core electrons, described in the same frozen wavefunctions. For the sake of simplicity we shall first consider hydrogen atoms, and a minimal basis set would be spanned by a single 1s AO per atom. For the H atom, the effective operator is $-0.5(\text{a.u.})|1s\rangle\langle 1s|$. For H_2 the model space is spanned by four determinants; calling a and b and $S^{-1/2}$ orthogonalized AOs $1s_A$ and $1s_B$ respectively, these four determinants are

$$\left.\begin{aligned}\phi_1 &= |a\bar{b}|\\ \phi_2 &= |b\bar{a}|\end{aligned}\right\}\text{neutral OVB components}$$

$$\left.\begin{aligned}\phi_3 &= |a\bar{a}|\\ \phi_4 &= |b\bar{b}|\end{aligned}\right\}\text{ionic OVB components}$$

$$P_0 = \sum_{i=1}^{4} |\phi_i\rangle\langle\phi_i|$$

as already discussed in Section III.C.2.

The first main problem concerns the choice of the target space. The (b) $^3\Sigma_u^+$ $||a\bar{b}| - |b\bar{a}||/\sqrt{2}$ combination will always correspond to the lowest (b) $^3\Sigma_u^+$ exact state, which dissociates into ground-state atoms. The ground state ($^1\Sigma_g^+$) has very large components in the model space, on neutral determinants only for large interatomic distances, and on neutral *and* ionic valence determinants at short interatomic distances. The two lowest eigenstates of H_2 should definitely belong to the target space.

For short interatomic distances the lowest (B)$^1\Sigma_u^+$ state is known to have

large components on the antisymmetric combination of ionic determinants $||a\bar{a}| - |b\bar{b}||/\sqrt{2}$, and it should therefore definitely belong to the target space. The model space contains a second $^1\Sigma_g^+$ state, a linear combination of valence neutral and ionic components, and one may assume that the fourth eigenstate of the target space is the lowest excited E ($^1\Sigma_g^+$) state. Thus

$$\begin{aligned} P = &|(\mathrm{X})^1\Sigma_g^+\rangle\langle(\mathrm{X})^1\Sigma_g^+| + |(\mathrm{E})^1\Sigma_g^+\rangle\langle(\mathrm{E})^1\Sigma_g^+| \\ &+ |(\mathrm{b})^3\Sigma_u^+\rangle\langle(\mathrm{b})^3\Sigma_u^+| + |(\mathrm{B})^1\Sigma_u^+\rangle\langle(\mathrm{B})^1\Sigma_u^+| \end{aligned} \tag{134}$$

P_0, P and the exact energies being known, the effective Hamiltonian is defined in one of its usual versions.

As a first remark, one should mention that the projections of the two $^1\Sigma_g^+$ states into the model space have no reason to be orthogonal, since in

$$\begin{aligned} &\psi(\mathrm{X})^1\Sigma_g^+ = \alpha(|a\bar{b}| + |b\bar{a}|) - \beta(|a\bar{a}| + |b\bar{b}|) + \cdots \\ &\psi(\mathrm{E})^1\Sigma_g^+ = \beta'(|a\bar{b}| + |b\bar{a}|) + \alpha'(|a\bar{a}| + |b\bar{b}|) + \cdots \\ &\qquad \alpha, \beta > 0 \end{aligned} \tag{135}$$

β' and β (resp. α' and α) are of the same order of magnitude but different. If $\beta'/a' = \beta/\alpha$ one might write

$$\begin{aligned} H^{\mathrm{eff}} = &E((\mathrm{b})^3\Sigma_u^+)[||a\bar{b}| - |b\bar{a}|\rangle\langle|a\bar{b}| - |b\bar{a}|| + ||ab|\rangle\langle|ab|| \\ &\qquad + ||\overline{ab}|\rangle\langle|\overline{ab}||] \\ &+ E((\mathrm{B})^1\Sigma_u^+)||a\bar{a}| - |b\bar{b}|\rangle\langle|a\bar{a}| - |b\bar{b}|| \\ &+ E((\mathrm{X})^1\Sigma_g^+)[|\alpha(|a\bar{b}| + |b\bar{a}|) - \beta(|a\bar{a}| + |b\bar{b}|)\rangle\langle\alpha(|a\bar{b}| + |b\bar{a}|) \\ &\qquad - \beta(|a\bar{a}| + |b\bar{b}|)|] \\ &+ E((\mathrm{E})^1\Sigma_g^+)[|\beta(|a\bar{b}| + |b\bar{a}|) + \alpha(|a\bar{a}| + |b\bar{b}|)\rangle\langle\beta(|a\bar{b}| + |b\bar{a}|) \\ &\qquad + \alpha(|a\bar{a}| + |b\bar{b}|)|] \end{aligned} \tag{136}$$

This will be the general expression of the Schmidt-orthogonalized effective Hamiltonian. If $\beta/\alpha \neq \alpha'/\beta'$, the Bloch effective Hamiltonian will be non-Hermitian. The relative advantages of the Bloch, des Cloizeaux, Schmidt-orthogonalized effective Hamiltonians, or of the intermediate Hamiltonians has never been tested, especially in transfers to large systems.

A second remark concerns the definition of the target space of large interatomic distances, and the occurrence of intruder states. For large enough interatomic distances the lower $(\mathrm{B})^1\Sigma_u^+$ state ceases to be valence (and ionic) to become of $\mathrm{H}(n=2) + \mathrm{H}(n=1)$ character. It dissociates into the H(2s) + H(1s) asymptote, i.e. an avoided curve crossing occurs between the ionic state and a Rydberg state. The same remark is valid for the second $^1\Sigma_g^+$ state, which is known to have two minima,[111] one of them being of Rydberg character. This state is only ionic for intermediate atomic distances, it is Rydberg on both short and large interatomic distances (cf. Fig. 10).

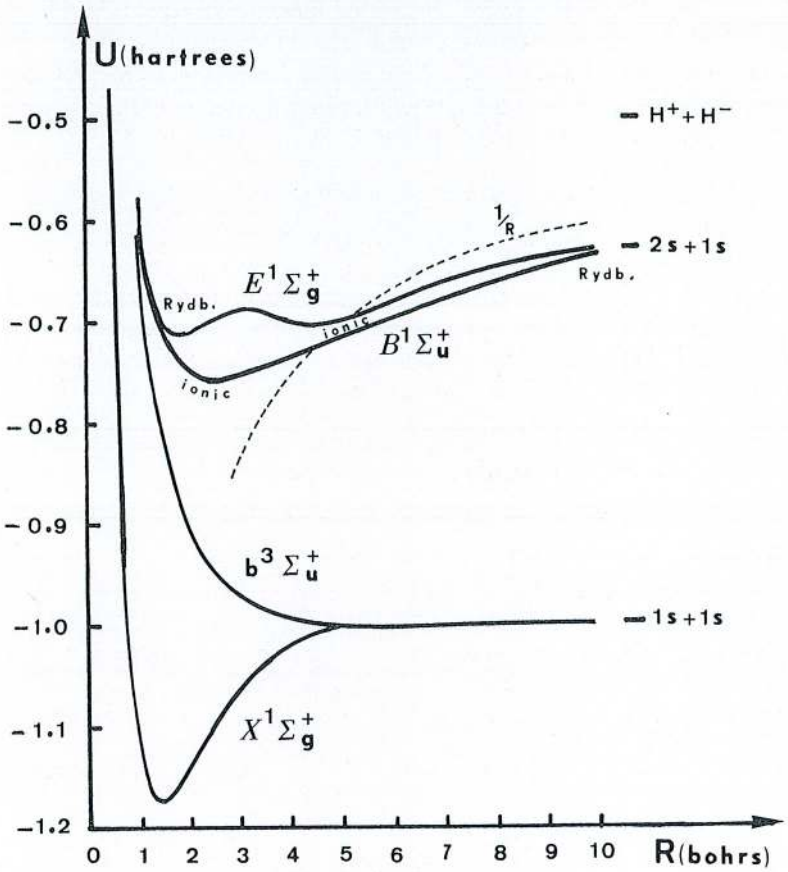


Fig. 10. Potential curves of the valence states of the H_2 molecule, showing the mixing with non-valence states.

Then one faces a dilemma:

1. One may either choose as target eigenvectors those which have the largest components onto the model space (maximum projection criterion) and in the $^1\Sigma_u^+$ symmetry, for instance, this eigenvector is the lowest $^1\Sigma_u^+$ root at short interatomic distances, then the second root besides a certain distance r_c, and may even go to the third root if a second Rydberg state appears below the ionic vector, etc. The problem is even worse with the $^1\Sigma_g^+$ symmetry. The consequence is that the effective Hamiltonian matrix elements are not continuous functions of the interatomic distances! The use of a discontinuous operator in larger systems (hydrogen clusters) seems to be very difficult.

2. One may forget this disappearance of the ionic components into higher eigenvectors and take an adiabatic definition of the target space assuming that the concerned roots are always the lowest of their symmetry, whatever their physical content. Then the effective operator matrix elements will be continuous functions of the interatomic distance, but the eigenvectors

$$\Phi_m = P_0 \psi_m$$

tend to have a vanishing amplitude when R_{AB} increases. This may result in numerical instability. It may also be dangerous to assume that in a cluster H_n a valence situation

$$H \cdots H^- \cdots H \cdots H \cdots H^+ \cdots H$$

will have the same energy as the situation

$$H \cdots H(2s) \cdots H \cdots H \cdots H(1s) \cdots H$$

6. *Transferability; Appearance of New Situations*

It one wants to treat an H_n problem using a bielectronic effective Hamiltonian derived from exact calculations on H_2, several questions arise concerning:

1. The choice of the basis set. One may perform a new $S^{-1/2}$ transform for the H_n conformation and identify the new orthogonalized AOs with that of the bicentric problem. This is the most direct solution but the orthogonalization tails will be different and the use in this new basis of the effective bielectronic Hamiltonian given in Eq. (136) for instance may result in uncontrolled effects. One may also express the bielectronic operator of Eq. (136) in the non-orthogonal basis set and calculate the Hamiltonian matrix of H_n in the basis of non-orthogonal determinants, antisymmetrized products of 1s AOs. The problem to solve is then of (*H-ES*) type and it faces a typical non-orthogonality problem of VB methods, which has been a major drawback of these approaches.
2. The occurrence of new situations. In a linear H system, for instance, one must consider (a) neutral determinants, for instance $|a\bar{b}c\bar{d}|$ or $|\bar{a}bc\bar{d}|$, etc.; (b) singly ionic determinants, some of them having dipoles between adjacent atoms ($|ab\bar{b}d|$, i.e. AB^-C^+D), while others introduce long-distance electron jumps ($|a\bar{a}b\bar{c}|$, i.e. A^-BCD^+); and (c) doubly ionic determinants such as $A^-B^+C^-D^+$ or $AA^-B^-C^+D^+$

One may wonder whether a bielectronic Hamiltonian extracted from the H_2 problem is able to deal with some of these situations and to assign reasonable energies to them. The neutral determinants only involve neutral–neutral

interatomic interactions which appeared in the H_2 problem. Assuming that

$$\langle a\bar{b}c\bar{d}|H^{\text{eff}}|a\bar{b}c\bar{d}\rangle = \langle a\bar{b}|H^{\text{eff}}|a\bar{b}\rangle + \langle ac|H^{\text{eff}}|ac\rangle + \langle a\bar{d}|H^{\text{eff}}|a\bar{d}\rangle + \text{etc.}$$

essentially neglects the possible three-body terms governed by the overlap expansion. But when one goes to singly ionic determinants in the energy of $|ab\overline{b'}d|$ (B^-C^+), while information concerning the B^-C^+ interaction or the AD interaction is contained in the H_2 effective Hamiltonian, information concerning the AB^- or the C^+D interactions are lacking. They should be extracted from H_2^- and H_2^+ problem respectively, i.e. from the one- and three-electron diatomic problems. This might be done in principle although one may notice that H_2^- is unbound at short interatomic distances, i.e. that it is impossible to define *exact* valence states of H_2^-.

The A^-BC^+D determinants involve strong polarizations of the intermediate B atom, which are not given by numerical transfers from A^-B or BC^+, due to the non-additivity of polarization energies.

When one goes to doubly ionic structures, $A^-B^-C^+D^+$ for instance, the relevant information concerning the A^-B^- interaction should be extracted from the H_2^{2-} valence state, which of course cannot be defined.

The transferability of a valence effective Hamiltonian defined on H_2 to H_n clusters therefore faces a series of basic difficulties, which leaves little hope of success. The situation would be even worse of course if one dealt with boron or carbon atoms since for C_2 already one should introduce strongly hybridized (for instance $C(p^4) + C(p^4)$) or multiply ionic (for instance $C^{4+} + C^{4-}(s^2p^6)$) states which are unbound. The choice of the target space is already impossible on the diatom, and the definition of an exact (Bloch, des Cloizeaux,...) effective Hamiltonian from knowledge of the spectrum of the diatom is either impossible or perfectly arbitrary. Even if it were possible, the treatment of B_4 or C_4 would introduce some multiply ionic valence ($C_4^{4+}C^{4-}C^{4-}C^{4+}$) determinants for which the assessment of an effective energy would be impossible.

There is thus little hope, in our opinion, for a rigorous definition of valence minimal basis set effective Hamiltonians. To build them, the use of the diatomic effective Hamiltonian may be useful, but some supplementary assumptions should be made, along a physically grounded model, to define for instance three-body polarization energies and the energies of highly hybridized or multi-ionic VB structures. One should realize the physical origin of these numerous troubles; they essentially come from the inclusion of the *ionic* determinants in the model space. This inclusion first resulted in intruder state problems for the diatom; it also leads to the appearance of multiply ionic structures in the valence minimal basis set space of the cluster. It seems that, even for H, the definition of a full valence space is too ambitious.

Besides the effort to give theoretical grounds (and non-empirical versions)

for the semi-empirical quantum chemistry or solid-state physics simplified Hamiltonians, which are valence minimal basis set Hamiltonians, Freed's attempt rested on a theoretical property, namely the size consistency (and the linked-cluster diagrammatic expansion) of the Rayleigh–Schrödinger QDPT development when the model space is a *complete* active space. The price to pay for the benefit of this theoretical guarantee is so large and so dramatic that one may wonder whether obtaining less ambitious effective Hamiltonians would not be preferable. (Notice that an effective Hamiltonian restricted to neutral non-hybridized plus neutral singly hybridized and singly ionic structures would be size-inconsistent, as is the double CI truncated treatment of the electronic correlation problem for the same fundamental reasons.)

This step towards simplification may proceed along two different ways:

1. One may resign oneself to treat the ionic states *exactly*, and use an intermediate Hamiltonian spanned by the *full* valence space but which concentrates on the neutral states and does not try to reproduce the ionic eigenstates. Work is in progress along this line; it shows that this approach solves many difficulties discussed above. The effective energies of the ionic determinants are not as critical, since they simply appear through their interaction with the neutral determinants to stabilize the lowest neutral states through electronic delocalization.
2. One may limit the model space to neutral situations. This is the philosophy of the Heisenberg Hamiltonians, which we discuss now.

D. Effective Hamiltonians Spanned by Neutral-only Valence-bond Determinants: Magnetic (Heisenberg) Hamiltonians and Their Possible Generalizations

The last class of effective Hamiltonians rests on the choice of a very limited model space, spanned by the neutral structures of an orthogonal VB development. This choice of the model space is grounded on the facts that (i) the neutral VB determinants are usually those of lowest energy, and (ii) the lowest eigenstates have large components on the neutral VB determinants. This model space is a part of the full valence space previously defined, and it is no longer a complete active space. The development of the corresponding effective Hamiltonians is especially simple for homogeneous systems involving only one type of active orbital (i.e. a single band), each atom having p electrons in p AOs (half-filled band). The simplest problem concerns systems where each atom brings one active electron in one AO. This is the case of clusters of hydrogen, alkali, or noble-metal atoms. The conjugated hydrocarbons may also be considered as belonging to that family if the active electrons are the π electrons, one per C atom in a $2p_z$ AO.

1. *Half-filled Bands with One Active Electron, One Atomic Orbital per Centre*

If a and b are two orthogonal localized orbitals of H (obtained for instance from the SCF calculation of the $(b)^3\Sigma_u^+$ state), the model space of neutral determinants is defined by

$$P_0 = ||ab|\rangle\langle|ab|| + ||\overline{ab}|\rangle + \langle|\overline{ab}|| + ||a\bar{b}|\rangle\langle|a\bar{b}|| + ||\bar{a}b|\rangle\langle|\bar{a}b| \quad (137)$$

Then, as previously discussed (see Section III.C.2) the most neutral eigenstates of 1s character are the ground $(X)^1\Sigma_g^+$ and lowest $(b)^3\Sigma_u^+$ states. Thus

$$P = |(b)^3\Sigma_u\rangle\langle(b)^3\Sigma_u| + |(X)^1\Sigma_g^+\rangle\langle(X)^1\Sigma_g^+| \quad (138)$$

where $(b)^3\Sigma_u^+$ involves its three $S_z = 0, \pm 1$ components.

Owing to space and spin symmetry, the eigenvectors projected into the model space are necessarily orthogonal

$$P_0|(b)^3\Sigma_u\rangle = \begin{cases} \|ab|\rangle & \text{for } S_z = 1 \\ \|\overline{ab}|\rangle & \text{for } S_z = -1 \\ (\|a\bar{b}|\rangle - \|b\bar{a}|\rangle)/\sqrt{2} & \text{for } S_z = 0 \end{cases}$$

$$P_0|(X)^1\Sigma_g^+ = (\|a\bar{b}|\rangle + \|b\bar{a}|\rangle)/\sqrt{2} \quad (139)$$

Then the effective Hamiltonian is entirely defined. It is Hermitian.

$$H^{\text{eff}} = E(^3\Sigma_u^+)[||ab|\rangle\langle|ab|| + ||\overline{ab}|\rangle\langle|\overline{ab}|| + ||a\bar{b}| - |b\bar{a}|\rangle\langle|a\bar{b}| - |b\bar{a}||] + E(^1\Sigma_g^+)||a\bar{b}| + |b\bar{a}|\rangle\langle|a\bar{b}| + |b\bar{a}|| \quad (140)$$

It may be written in second quantization form

$$H^{\text{eff}}(a,b) = E(^3\Sigma_u^+)_{ab} + [E(^1\Sigma_g^+)_{ab} - E(^3\Sigma_u^+)_{ab}] \cdot (a_a^+ a_{\bar{b}}^+ + a_b^+ a_{\bar{a}}^+)(a_{\bar{b}} a_a + a_{\bar{a}} a_b) \quad (141)$$

There are only two parameters in the model, $E(^3\Sigma_u^+)$ and $E(^1\Sigma_g^+)$, which are distance-dependent, and may be expressed as

$$R(r_{ab}) = E(^3\Sigma_u^+)$$
$$g(r_{ab}) = \tfrac{1}{2}[E(^1\Sigma_g^+) - E(^3\Sigma_u^+)] \quad (142)$$

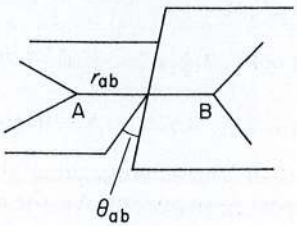
r_{ab} being the interatomic distance.

For the isoelectronic problem of the ethylene molecule, where the model space is reduced to two determinants having the same $\phi_c\sigma$ core

$$\phi_1 = |\phi_c \cdot a| \qquad \phi_2 = |\phi_c \cdot b| \quad (143)$$

a and b are now $2p_z$ AOs on atoms A and B, and the target eigenstates are the $X(^1A_1)$ ground state and the lowest $(^3B_2)$ $\pi\pi^*$ triplet state. The two basic parameters are then functions of both the r_{ab} distance and the torsional angle

around the C–C bond θ_{ab}:



$$R(r_{ab}, \theta_{ab}) = E(^3B_2) \tag{144}$$

$$g(r_{ab}, \theta_{ab}) = \tfrac{1}{2}[E(^1A_1) - E(^3B_2)] \tag{145}$$

(Other parameters such as the pyradimalization angle of a C atom might be considered as well.)

Since the two determinants of the model space have the same space part and only differ by their spin, the effective Hamiltonian may be written as a spin-dependent Hamiltonian, the space part becoming implicit, but well defined (close to that of the separate atoms). A direct algebraic derivation shows that, if one defines E_0 as the barycentre of the configuration (which includes three triplets and one singlet),

$$E_0 = [3E(^3\Sigma_u^+) + E(^1\Sigma_g^+)]/4 \tag{146}$$

it becomes possible to write Eq. (141) as

$$H_{ab}^{\text{eff}} = E_0 + 2g\mathbf{S}_a \cdot \mathbf{S}_b \tag{147}$$

where $\mathbf{S}_a$ is the spin angular momentum on atom A, and g may be seen as an effective exchange integral.

One recognizes here the expression of a magnetic or Heisenberg Hamiltonian.[112] Heisenberg Hamiltonians were first proposed as phenomenological Hamiltonians and used to fit[113,114] the spectroscopic splittings between the multiplets of atoms or of molecular systems having several centres with unpaired electrons. Anderson[81] (see also Ref. 115) recognized that the Heisenberg Hamiltonians might be understood as effective Hamiltonians, deduced from the exact Hamiltonian by the choice of a model space reduced to the neutral VB components of the system of n electrons in n AOs. For a problem with two electrons, two AOs and two centres, the amplitude of the magnetic coupling $2g$ is directly reducible to the gap between the lowest singlet and triplet states (Eq. 145)); when working in an orthogonal basis set, this difference is known to come from the mixing between neutral and ionic components, which occurs in the singlet manifold, while it is impossible for the triplet stage. Turning back to the 4×4 matrix (Eq. (114)), it is clear[116,117] that after symmetry transformations and diagonalization of the 2×2 matrix

concerning the $^1\Sigma_g^+$ symmetry

$$E(^3\Sigma_u^+) = -K_{ab} \tag{148}$$

$$E(^1\Sigma_g^+) = K_{ab} + \tfrac{1}{2}[\Delta E - (\Delta E^2 + 16F^2)^{1/2}] \tag{149}$$

i.e.

$$2g = 2K_{ab} - \Delta E - (\Delta E^2 + 16F^2)^{1/2} \tag{150}$$

where K_{ab} is the direct (first-order) exchange integral between the a and b AOs, F the hopping integral between them, and ΔE the energy difference between neutral and ionic determinants. If $|F| \ll \Delta E$, one may write

$$g = K_{ab} - 2F^2/\Delta E \tag{151}$$

K_{ab} is always positive. It lowers the triplet state energy and is said to be *ferromagnetic*. The second term lowers the singlet state and is called *antiferromagnetic*; and in most cases it predominates over the direct exchange, most systems therefore being antiferromagnetic.

Equation (151) may be obtained directly in a second-order (Q)DPT derivation of an effective Hamiltonian spanned by $|a\bar{b}|$ and $|b\bar{a}|$, and where the ionic determinants $|a\bar{a}|$ and $|b\bar{b}|$ span the outer space

$$\begin{aligned}\langle |a\bar{b}\| H^{\text{eff}} \| a\bar{b}| \rangle &= K_{ab} - \langle |a\bar{b}\| H \| a\bar{a}| \rangle \langle |a\bar{a}\| H \| a\bar{b}| \rangle / \Delta E \\ &\quad - \langle |a\bar{b}\| H \| b\bar{b}| \rangle \langle |b\bar{b}\| H \| bb| \rangle / \Delta E \\ &= K_{ab} - 2F^2/\Delta E \end{aligned} \tag{152}$$

$$\begin{aligned}\langle |a\bar{b}\| H^{\text{eff}} \| b\bar{a}| \rangle &= K_{ab} - \langle |a\bar{b}\| H \| a\bar{a}| \rangle \langle |a\bar{a}\| H \| b\bar{a}| \rangle / \Delta E \\ &\quad - \langle |a\bar{b}\| H \| a\bar{b}| \rangle \langle |b\bar{b}\| H \| b\bar{a}| \rangle / \Delta E \\ &= K_{ab} - 2F^2/\Delta E \end{aligned} \tag{153}$$

This perturbative approach is of course only valid when $|F|/\Delta E \ll 1$, i.e. when the electronic delocalization, governed by F, is smaller than the increase in the electronic repulsion when going from neutral to ionic determinants

$$\begin{aligned}\Delta E &\simeq J_{aa} - J_{ab} \\ &= U \qquad \text{in the Hubbard Hamiltonian}^{116}\end{aligned}$$

The outer space may be extended to any kind of determinant, involving angular and radial correlations of the ionic pairs $|a\bar{a}|$, or instantaneous repolarizations of the core in the ionic structures, as discussed in Section III.C.2. It becomes possible to treat these effects, which are additional to the second-order correction, as a dressing of the ionic structure energy, i.e. as a change of ΔE

$$\Delta E \to \overline{\Delta E} = \Delta E - \sum_{\sigma} \frac{\langle \sigma | J_a - J_b | \sigma^* \rangle^2}{\Delta E'} - \sum_{a_i' a_i''} \frac{(aa_i', aa_i'')^2}{\Delta E''} \tag{154}$$

through infinite summations of diagrams.[117]

We would like to stress the fact, however, that the convergence of the (Q)DPT perturbation expansion is by no means necessary to define a Heisenberg Hamiltonian, which is perfectly defined by the model space, the target space and the corresponding eigenenergies, all of which are known unambiguously in this precise problem. The possibility to define a Heisenberg Hamiltonian is *not* restricted to the case $|F| \ll \Delta E$, i.e. to problems which are weakly delocalized or strongly correlated, as usually believed.

a. Transfer

One may be tempted to transfer the Heisenberg Hamiltonian from the diatom to a cluster of atoms, or from ethylene to larger conjugated molecules,[118–128] i.e. to write

$$H^{\mathrm{T}} = \sum_{i,j} H_{ij}^{\mathrm{eff}} \tag{155}$$

This Hamiltonian will act on the neutral OVB determinants of the cluster, the space part of which are identical to the product of the valence AOs (i) centred on the various atoms (I), and supposed to be orthogonal. The various determinants differ by the spin distribution

$$\phi_K = \left(\prod_I i\right)\left(\prod_I \sigma_{iK}\right) \tag{156}$$

where σ_{iK} is the spin (α or β) borne by the atom I in the determinant ϕ_K. For the $S_z = 0$ (resp. $\frac{1}{2}$) manifold, which contains all possible multiplets of the problem, in a $2n$ (resp. $2n+1$) centre problem, the size of the model space is C_{2n}^n (resp. C_{2n+1}^n), i.e. the number of ways to put n electrons on $2n$ (resp. $2n+1$) centres.

This size is much smaller than that of the full VB matrix in the same minimal basis set, an of course fantastically smaller than the size of the CI in a large basis set. The treatment can of course only give *neutral* eigenstates, i.e. those which have *the largest projections onto* the neutral determinant subspace. Notice that this sentence has a very precise meaning; it does not mean that the corresponding eigenstates have a larger component into the model space than on the outer space; $\langle \psi_m | P_0 \psi_m \rangle$ may be smaller than $\langle \psi_m | Q_0 \psi_m \rangle$ as easily seen by considering $n\mathrm{H}_2$ diatoms at infinite distances: if for H_2

$$\langle \psi(^1\Sigma_g^+) | P_0 \psi(^1\Sigma_g^+) \rangle = \alpha \tag{157}$$

for $(\mathrm{H}_2)_n$

$$\langle \psi_0 | P_0 \psi_0 \rangle = \alpha^n \ll 1 - \alpha^n \qquad \text{for } n \text{ sufficiently large}$$

The Heisenberg Hamiltonian, of course, cannot deliver the energies of the states which are essentially ionic. It cannot give the energy of the lowest excited singlet state of H_2 (dipole-allowed $^1\Sigma_u^+$) nor the lowest $^1\mathrm{B}_2$ ($\pi\pi^*$) singlet state

of ethylene. The lowest dipole-allowed singlet states of conjugated hydrocarbons are essentially ionic and they cannot be reached by such an effective Hamiltonian.

The legitimacy of the transfer from the two-centre to the n-centre problem may be discussed along two lines:

1. As previously discussed in Section III.C, about the transferability of the valence minimal basis set effective Hamiltonians, the orthogonal valence AOs are not he same in the two-centre and n-centre problems, due to large orthogonalization tails if one uses $S^{-1/2}$ procedures, or to many-body distortions if one uses the localized MOs of the upper valence multiplet.[81] But it has been noticed[127] that the two-centre Heisenberg Hamiltonian is *entirely determined by symmetry, the amplitude of its operators being independent of the precise content of the two orthogonal valence orbitals a* and *b*. One may thus define truncated *ad hoc* AOs with weak (or even zero) spatial overlap. In that precise case the model space AOs are transferable. The second-order corrections inducing spin exchanges between atoms B and C in an ABCD cluster are identical to those concerning the BC spin exchange in the BC diatom. The same is true for higher-order terms involving only the two *ad hoc* valence AOs *b* and *c*.
2. Many-body (i.e. many-centre) terms would appear[112] if one derived directly the effective Hamiltonian spanned by the neutral OVB determinants of the H_n problem. Even the two-body terms between, say, two determinants differing by a spin exchange between atoms B and C in an ABC cluster will be different from the effective exchange in the BC diatom

$$\langle |a\bar{b}c\bar{d}| \| H^{\text{eff}}_{\text{ABCD}} \| a\bar{b}\bar{c}d| \rangle \neq \langle |b\bar{c}| \| H^{\text{eff}}_{\text{BC}} \| b\bar{c}| \rangle$$

due to perturbation orders larger than two, which imply for instance A^-C^+ singly ionic determinants between non-adjacent atoms, which do not appear in the BC problem. This question has been well studied by Maynau *et al.*[123,124,128] on model problems (i.e. starting from a PPP type Hamiltonian of π systems). They concluded that

   a. two-body terms are quite transferable,
   b. three-body terms are negligible,
   c. four-body terms are large in compact (square) structures and negligible when the four atoms do not define a cyclic structure, and
   d. six-body terms are lower than four-body terms but remain significant for cyclic structures.

The Heisenberg Hamiltonians should therefore include many-spin operators, which are essentially functions of the $|F|/\Delta E$ (i.e. β/U) ratio. The derivation of spin effective Hamiltonians is again always possible, whatever the $|F|/\Delta E$ ratio, but the negligibility of many-spin (>2) operators is only

valid for small $|F|/\Delta E$ values, i.e. for the highly correlated case, at least in compact structures. This restriction is not valid for systems involving only linear or branched chains or large cycles.

The most convincing applications of Heisenberg Hamiltonians in chemistry concern the X_3 problem (X being an H or alkali atom),[130] for which the two-body Heisenberg Hamiltonian is very efficient in predicting geometries and energies, and conjugated hydrocarbons. In a series of papers[123–126] it has been shown that most chemical concepts for these problems might be translated in terms of spin organization. Even the Woodward–Hoffmann rules may be demonstrated in this language where they concern the cyclic many-body operators. A careful extraction of the R and g parameters from accurate MO-CI calculations on ethylene as functions of bond distance and torsion angle gives a fantastically cheap and accurate tool[124,125] in the simplest two-body version of the Heisenberg Hamiltonian. Geometries are provided within 0.015 Å; the isomerization enthalpies and the rotational barriers are excellent; the transition energies towards neutral excited states are in very good agreement with the experimentally known values; and the model is able to treat the geometry reorganizations in neutral excited states, which are so difficult to calculate in MO-CI calculations. The open-shell problems are as easy to treat as are the closed-shell ones. The simplicity of the Heisenberg Hamiltonian has made possible research on asymptotic laws[125–127] for linear or cyclic polyenes concerning bond alternation, rotational barriers, solitonic deformation and excitation energies to the lowest triplet state (or lowest doublet excited state). The fantastic successes of these approaches—completely foreign to the conceptual background of chemistry—is in strong contrast with the difficulties encountered in research on valence-only effective Hamiltonians.

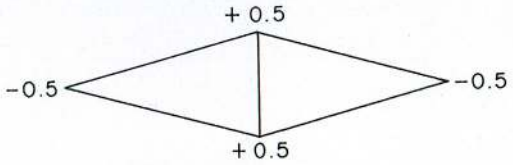
The model has even been used with success for the study of nitrogen-containing conjugated systems, $>C{=}N-$bonds, i.e. weakly polar molecules[131,132] and is being extended to $>C{=}O$ containing systems.

The number of systems defining a half-filled band with one e^-, one AO per centre is however very limited. The alkali-metal and noble-metal clusters and solids belong to this category, but they are conducting metals and it seems risky to treat a conducting metal through a model that has been developed especially for a peculiar class of insulators (Mott insulators), which only treats explicitly neutral structures, in which each atom of the lattice keeps one electron. This challenge has been attempted, however, by Malrieu *et al.*,[129] who extracted accurate two-body Heisenberg Hamiltonians from the diatom lowest potential curves, and treated the solid by perturbing the spin wave presenting the largest number of spin alternacy between neighbouring atoms. This zeroth-order wavefunction is perturbed to fourth order by the spin exchanges. One may optimize the lattice parameters and compare the cohesive energy of various crystalline lattices. The results are surprisingly good,

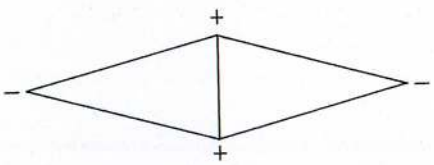
concerning the preferred crystallization mode (b.c.c. $\simeq$ compact ones for Na, Li, compact forms more stable than b.c.c. for Cu), the lattice parameters, the cohesive energy and even the bulk modulus (compressibility).

This highly unorthodox model of the conducting solid cannot explain the conductivity, although it is not incompatible with it since the wave operator Ω would build ionic components from the projected (neutral-only) wavefunction. From the principles, and as shown by the previously mentioned success of Heisenberg Hamiltonians on the most metallic chemical systems (aromatic molecules), almost any system of which the lowest VB determinants are neutral may be treated either by the independent-particle approach followed by a treatment of electronic correlation which reduces the ionic components[133,134] or by a Heisenberg-type effective Hamiltonian. This statement seems to be true whatever the β/U ratio. Malrieu *et al.*[129] also noticed that the many-body effects (for instance four-body cyclic contributions), which are so important on small molecules and clusters, play a much less important role in the solid.

One should point out, however, that the Heisenberg Hamiltonian fails to predict correctly the planar rhombus structure of Li_4 (and Na_4 or Cu_4) clusters. This failure has two origins: one is the involvement of the p band, which begins to be significantly populated in X_4 systems; the other is the highly ionic character of the ground state in its rhombus equilibrium geometry



where the short diagonal has almost lost one electron. This means that the



di-ionic component is quite low in energy, and the problem apparently cannot be treated by taking a model space of neutral VB structures. This opens two general questions concerning conducting solids: (i) Are the lowest-energy VB determinants the neutral ones? Might not multiply and regularly ionized determinants be lower in energy, if the + and − atoms regularly placed along a sublattice induce a stabilizing Madelung's field and polarize the neutral atoms? (ii) Is the Hubbard Hamiltonian, generally used to treat the correlation effects in solids, relevant since it cannot take into account this collective electrostatic stabilization?

These fundamental questions regarding the description of the simplest metals are actually fascinating and a major challenge on the borderline between quantum chemistry and solid-state physics.

2. *Half-filled Band with p Electrons in p Atomic Orbitals per Centre*

It might be thought that the foundation of Heisenberg Hamiltonians for half-filled bands where each atom brings p electrons in p AOs is evident. The Heisenberg Hamiltonian would distinguish intra-atomic (generally ferromagnetic, due to Hand's rule) and inter-atomic (generally antiferromagnetic) effective exchanges

$$\begin{aligned} H^{\text{eff}} &= \sum_{AB} R_{ab} + \sum_{A} \sum_{i_A j_A} K_{i_A j_A} (a_{j_A}^{+} a_{\bar{j}_A}^{+} + a_{j_A}^{+} a_{\bar{i}_A}^{+} (a_{\bar{j}_A} a_{i_A} + a_{\bar{i}_A} a_{j_A}) \\ &\quad + \sum_{AB} \sum_{i_A} \sum_{j_A} g_{i_A j_B} (a_{i_A}^{+} a_{\bar{j}_B}^{+} + a_{j_B}^{+} a_{\bar{i}_A}^{+}) (a_{j_B} a_{i_A} + a_{i_A} a_{j_B}) \\ &= E_0 + \sum_{ij} g_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \end{aligned} \tag{158}$$

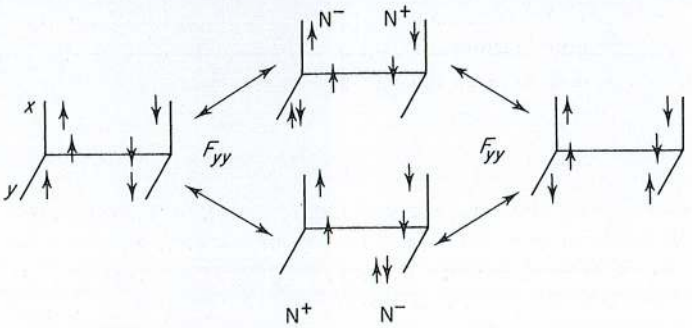
In general the atomic orbitals i_A and j_A on the same centre are orthogonal by symmetry. As examples of half-filled bands, one might consider a cluster of nitrogen (N) atoms, keeping the s^2p^3 configuration with one electron in each p_x, p_y, p_z AO, as occurs in the free atom ground state. Then in N, the p_x, p_y and p_z AOs belong to three different symmetries (π_x, π_y and σ) and

$$\langle i_A | F | j_A \rangle = \langle i_A | F | j_B \rangle = 0 \qquad \text{if } i \neq j$$

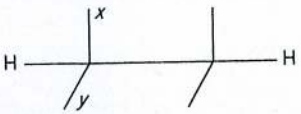
The only hopping integrals occur between AOs of the same molecular symmetry ($\langle i_A | F | j_A \rangle \neq 0$) and Anderson's delocalization mechanism will take place within each symmetry subspace. The integrals $K_{i_A j_A}$ are essentially first-order terms, responsible for the atomic preference for high-spin order (the ground state of N is (^{4}S), i.e. $s^2 p_x p_y p_z$) while the interatomic effective exchange will again come from the second-order coupling between the neutral and singly ionic determinants; for instance for $S_z = 0$

$$\begin{aligned} &\langle s_A^2 x_A y_A z_A s_B^2 \bar{x}_B \bar{y}_B \bar{z}_B | H^{\text{eff}} | s_A^2 x_A \bar{y}_A z_A s_B^2 \bar{x}_B y_B \bar{z}_B \rangle = (y_A y_B, y_A y_B) \\ &\quad + \langle s_A^2 x_A y_A z_A s_B^2 \bar{x}_B \bar{y}_B \bar{z}_B | H | s_A^2 x_A y_A \bar{y}_A z_A a_B^2 \bar{x}_B \bar{z}_B \rangle (\Delta E_{y_A \leftarrow y_B})^{-1} \\ &\qquad \times \langle s_A^2 x_A y_A \bar{y}_A z_A s_B^2 \bar{x}_B \bar{z}_B | H | s_A^2 x_A \bar{y}_A z_A s_B^2 \bar{x}_B y_B \bar{z}_B \rangle \\ &\quad + \text{inverse } (y_A \rightarrow y_B) \text{ term} \\ &\quad = (y_A y_B, y_A y_B) + 2F_{y_A y_B}^2 / \Delta E_{y_A \rightarrow y_B} \end{aligned} \tag{159}$$

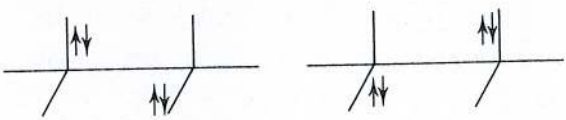
where the interatomic direct exchange integral is very small, while the second term is due to the electronic delocalization in the π_y subsystem. Maynau



et al.[135] have tried to analyse the effect of higher orders on a problem involving two electrons and two orthogonal AOs per centre, namely the acetylene π problem when the σ core is taken frozen. Using accurate large basis set

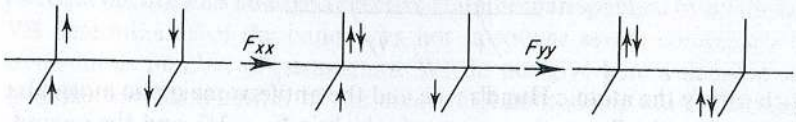


MO-CI wave functions, they noticed that the Bloch effective hamiltonian was highly non-Hermitian, and that its diagonal energies did not follow the Heisenberg structure. The des Cloizeaux effective Hamiltonian also deviated strongly from the structure of a Heisenberg Hamiltonian. Both the Bloch and des Cloizeaux effective Hamiltonians when transferred into the upper homologue (H—C˙=C=C˙—H) were unable to predict correctly the ground-state nature. In contrast with these failures, the Schmidt-orthogonalized effective Hamiltonian appeared to keep the Heisenberg structure and predicted correctly the lower parts of the linear HC_3H molecule. The reasons for these unexpected results were analysed, and were shown to be due to the occurrence of low-lying neutral VB vectors in the outer space. For the acetylene problem these states are $x_A^2 y_B^2$ and $y_A^2 x_B^2$. They have a different



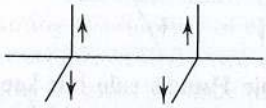
space part than $(\sigma)x_A y_A x_B y_B$ and they cannot therefore enter the model space generating a spin-only effective Hamiltonian. These determinants are neutral, the atoms are no longer in their ground state, but such VB structures are quite low in energy, and they will act as intruder states. They appear at second order

in the wavefunction expansion through processes like



(160)

i.e. with a large coefficient. Note that the model space necessarily involves situations of the type

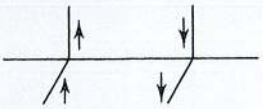


in which the overlapping AOs (x_A, x_B) and (y_A, x_B) have the same spin, and therefore do not permit any delocalization. These determinants, coupled with the lower ones through the *intra*-atomic spin exchange, are higher in energy than the neutral VB determinants belonging to the outer space. This generates trouble in the perturbation expansion and non-orthogonality between the projections of the eigenfunctions $\langle \Phi_m | \Phi_n \rangle \neq 0$ in the $^1\Sigma_g^+$ symmetry, due to strong components of the second and third eigenvectors on the (model space)$|x_A \bar{y}_A x_B \bar{y}_B|$ and (outer space)$|x_A \bar{x}_A y_B \bar{y}_B| VB$ components. This analysis shows that, for systems where each atom brings more than one active electron in one AO, (i) the perturbative (QDPT) generation of the Heisenberg Hamiltonian would diverge (the second-order result, which gives the expected Heisenberg structure, can only be considered as asymptotic), and (ii) the Heisenberg Hamiltonian is obtained from the Schmidt orthogonalization of the projections Φ_m of the eigenvectors into the model space (i.e. one accepts to lose more information on the upper eigenvectors than on the lowest ones, as seems reasonable). The same Heisenberg structure is obtained by using the intermediate Hamiltonian theory.[34]

3. *Non-heisenberg Effective Hamiltonians Spanned by All Neutral Valence-bond Structures for Half-filled Bands*

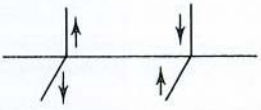
An attractive solution[136] would simply consist of enlarging the model space, leaving the constraint that all its determinants have the same $x_A y_A x_B y_B$ space part with one electron per active AO. If one includes the neutral VB determinants with zero or two electrons in the same AO, i.e. the determinants which acted previously as intruder states, one enlarges the model space, and one also introduce states of a different space part. For C_2H_2 again the Heisenberg Hamiltonian was spanned by six determinants (for $S_z = 0$) of three types, namely

1.



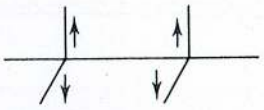
which satisfy the atomic Hund's rule and the antiferromagnetic molecular arrangement, the first-order energy of which is $E_0 - 2K$, and the second-order energy $E_0 - 2K - 2g$;

2.



which do not satisfy the atomic Hund's rule but keep the bond antiferromagnetic alignment, the first-order energy of which is E_0, and the second-order energy $E_0 - 2g$;

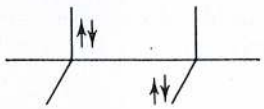
3.



which do not satisfy neither the atomic Hund's rule nor the bond antiferromagnetism, and have an energy E_0 at both first and second orders.

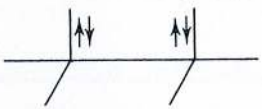
Then one must add two types of determinants:

4.



which have a first-order energy $E_0 + 2U$, due to the repulsion of the electrons in the same AO, and a second-order energy $E_0 + 2U - 2g$; and

5.



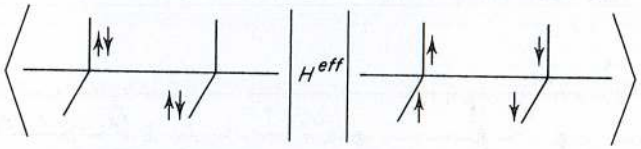
which do not permit electron delocalization, remaining very repulsive, with an energy $E_0 + 2U$.

Notice that in a minimal basis set $U = 2K$ and the coupling between the last two types of determinants is $K(\langle x_A^2 y_B^2 | H | x_A^2 y_A^2 \rangle = K_{xy})$, so that the number of parameters is not enlarged at this low order of perturbation. The coupling between the neutral (0 or 2 e^- per AO) determinants and those spanning the Heisenberg Hamiltonian (1e^- per AO) occurs at the second order, as already mentioned (cf. Eq. (160)), and its magnitude is $2F_{xx}F_{yy}/\Delta E$, i.e. $2F^2/\Delta E = g$ if the

two subsystems π_x and π_y are equivalent (or $\sqrt{(g_x g_y)}$ if the two subsystems are not equivalent). This enlarged effective Hamiltonian spanned by *all* the neutral VB determinants of the band does not introduce severe complexity and a tremendous number of parameters. We do not give here a detailed second quantization formulation of the effective Hamiltonian, which belongs to a more general category given below, but one may say that it introduces some operators

$$\sum_i U_i(a_i^+ a_{\bar{i}}^+ a_{\bar{i}} a_i)$$

i.e. an operator counting the number of electron pairs in the same AO and terms involving *four* atomic orbitals, two of them belonging to atom A and two of them belonging to atom B, since the extradiagonal terms



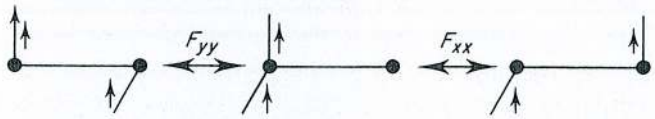
for instance, involve *four* AOS.

This effective Hamiltonian, which may be seen as a generalized Heisenberg Hamiltonian, since it is inspired by the same philosophy, solves some previously mentioned intruder states and thus convergence difficulties since it includes the intruder states of the strict Heisenberg Hamiltonian in its enlarged model space. One should note, however, that the price to pay is the inclusion of the strongly repulsive $|x_A^2 x_B^2|$ determinants in the model space, which may in turn introduce other intruder states (for instance $\sigma \rightarrow \sigma^*$ excited determinants).

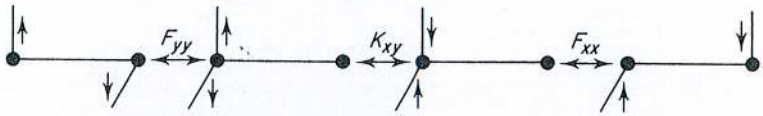
4. *Non-half-filled Bands: Example of Systems Having One Electron in p Atomic Orbitals per Centre (Magneto-angular Effective Hamiltonians)*

Up till now we have only considered half-filled bands. One might wonder whether the basic idea which leads to Heisenberg Hamiltonians might not be generalized, again considering a model space spanned by the neutral VB determinants, even when these determinants do not have the same space part. The simplest problem concerns atoms having one valence electron which can occupy *p* equivalent AOs (i.e. degenerate in the atom and thus belonging to the same band). As a tentative example[137] one may consider for instance B atoms, keeping an s^2p character, where each atom has only one 2p electron which can occupy one of the three p_x, p_y, p_z AOs. There are thus two degrees of freedom, the space angular momentum of each atom, and its spin momentum. The 'radial' parts of the molecular wavefunctions of the model space are identical and one may immediately see that the effective Hamiltonian will be a *magneto-*

angular effective Hamiltonian. This has been proposed by Marinelli *et al.*,[137] who analysed the problem on the B_2 diatom, derived an 'exact' effective Hamiltonian from accurate large basis set MO-CI calculations and tested its transferability to the B_3 linear molecule. The effective interactions may concern four AOs, for instance the space part of atoms A and B are changed in the second-order coupling between the two determinants spanning the $^3\Sigma_u^-(S_z = 1)$ ground state

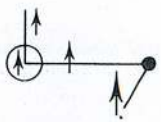


(where ● represents one $(2s)^2$ electron pair). The third-order corrections, for instance



change both the space and spin parts of the atoms; they are however less important. The 'exact' effective Hamiltonian does not deviate strongly from the *structure* predicted by the low-order expansion although the terms appearing at order larger than 2 are damped with respect to their theoretical value.

The model space for B_2 does not span the state $^5\Sigma_g^-$ which is nearly degenerate with the $^3\Sigma_u^-$ ground state; the $^5\Sigma_g^-$ state is spanned by hybridized VB determinants involving the lowest excited state (sp^2) of one atom $s_A z_A x_A$ and a ground-state atom $s_B^2 y_B$

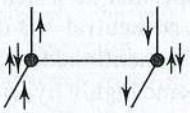


(where ○ represents the 2s AO). Despite this near-degeneracy, the effective Hamiltonian was able to predict correctly the ordering and spacing of the four lowest states of the B_3 linear molecule, independently determined by accurate MO-CI calculations. The model suggests that the linear B_n chain might be ferromagnetic.[137]

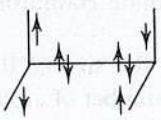
The remark concerning the low-lying hybridized state questions, however, the reliability of effective Hamiltonians spanned by the neutral non-hybridized OVB determinants, i.e. involving a single band.

5. *General Effective Hamiltonians Spanned by All Neutral OVB Determinants, and Involving Several Bands*[138]

In a further step to generalize the Heisenberg Hamiltonians, one may decide that they will be spanned by all the possible OVB valence neutral determinants, without any assumption concerning their hybridization state. The carbon atom will be either s^2p^2, sp^3 or p^4 for instance. In the language of solid-state physics, one would say that the two bands s and p are both involved. The various zeroth-order energies of the determinants belonging to the model space are no longer degenerate, since in C_2, for instance, the VB determinant $s_A^2 x_A y_A - s_B^2 \bar{x}_B \bar{y}_B$,

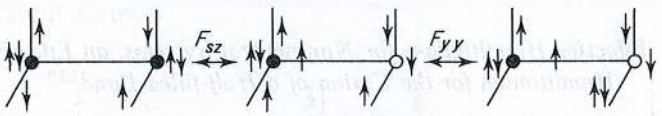


in which both atoms are in their atomic ground state, is much lower in energy than the determinant $p_{x_A} p_{y_A} p_{z_A}^2 \overline{p_{x_B} p_{y_B}} p_{z_B}^2$



in which both atoms are excited and which induces large interatomic repulsions in the σ symmetry.

One should therefore introduce mono- and bielectronic diagonal terms which take into account both the spectroscopic state of the atom and the interatomic repulsion energies, which depend on the orbital occupancies. The second-order Anderson-type corrections would then concern all back-and-forth processes from a neutral to a neutral OVB determinant through a singly ionic VB determinant. For instance in C_2, the second-order process



involving four AOs through an $A \leftarrow B$ electron jump followed by an $A \rightarrow B$ reverse electron jump, may be seen as a generalization of Anderson's process leading the antiferromagnetic effective exchange in a half-filled band.

The general back-and-forth operators may be written

$$(i_A j_B, k_A l_B)^{\text{eff}} (a_{i_A}^+ a_{j_B})(a_{l_B}^+ a_{k_A})$$

where

$$(i_A j_B, k_A l_B)^{\text{eff}} \simeq 2F_{i_A j_B} F_{k_A l_B}/\Delta E \tag{161}$$

where i_A, j_B, k_A, l_B are now *spin orbitals*. Notice that one may have $j_B = l_B$, $i_A = k_A$, i.e. diagonal corrections. The problem concerns the definition of ΔE, which should be the energy of the two intermediate (singly ionic) outer determinants, with respect to the ket neutral determinant, in a Bloch-type expansion. The non-degeneracy of the model space, due to the hybridization, leads to the already discussed non-hermiticity problems. These problems may certainly be solved either through the hierarchic (i.e. Schmidt-type) orthogonalization procedure of the projected eigenvectors Φ_m or by the use of an intermediate Hamiltonian approach in which the main model space would only involve the non-hybridized neutral VB determinants.

Two other difficulties must be mentioned, namely (i) the possible occurrence of ionic intruder states since some highly hybridized neutral VB determinants may be high in energy, and (ii) the difficulty of calculating and selecting the set of exact wavefunctions ψ_m to define the target space, if one wants to use an *a posteriori* definition of the effective Hamiltonian, from knowledge of the target space.

Again the use of an intermediate Hamiltonian formalism may solve these difficulties.

The last problem concerns the size of the model space, which rapidly becomes very larger when the number of atoms increases and new approximations would certainly be required.

One may nevertheless think that the above-mentioned strategy, which generalized Anderson's derivation of the Heisenberg Hamiltonian, is both conceptually interesting and practically useful especially if some simple parametrized formulae were used to obtain the effective integrals. Work is under progress[138] to define some Anderson–Hoffmann model where the diagonal energy differences (and monocentric exchanges) would be taken from the atomic spectra, the repulsive terms would be simple functions of interatomic overlaps and distances, and the effective bielectronic terms would be governed by simple AO overlap dependences.

6. *Effective Hamiltonians for Non-neutral Systems; an Effective Hamiltonian for the Cation of a Half-filled Band*[139]

So far the systems under study in this section have been neutral, and the effective VB was spanned by the neutral VB determinants. One might wonder whether it would not be possible to treat a non-neutral system in a similar way. To do this one must again consider among the OVB determinants those which have the lowest energy. While for neutral systems one had an energetic hierarchy according to the inonicity of the determinants

$$\text{neutral} < \text{singly ionic} < \text{doubly ionic} < \cdots$$

for the cations one may introduce the following hierarchy of determinants

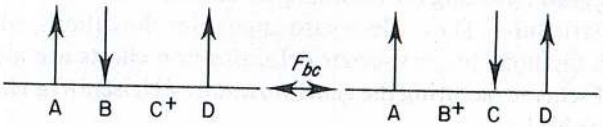
$$\text{one hole} < \text{two holes} < \text{three holes} < \cdots$$

The holes are the number of atomic positive charges. A two-hole determinant necessarily involves two positively charged atoms or an atom bearing two positive charges, and another atom bearing one negative charge.

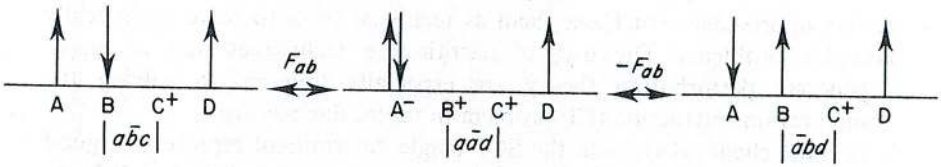
The simplest problem again concerns the cations of a half-filled band, for instance the cations of conjugated molecules, for which one may consider an $S_z = 0$ (or $\frac{1}{2}$) model space of dimension

$$n \times C_{n-1}^{(n-1)/2}$$

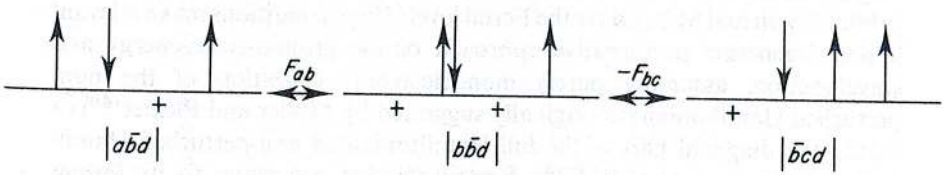
since each atom may be positively charged, the other atoms bearing one electron of α or β spin. This dimension is larger than that of the neutral problem. The effective Hamiltonian involves first-order hopping integrals between determinants differing only by the hole, for instance between $|a\bar{b}d|$ and $|a\bar{c}d|$ in $[ABCD]^+$



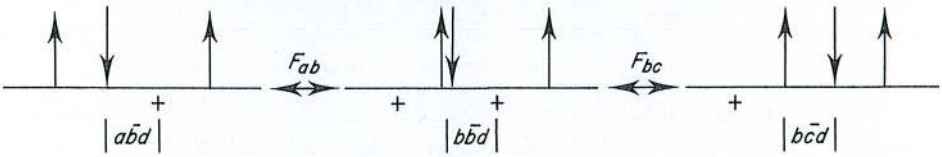
Second-order effective exchanges occur, as in neutral systems, between atoms which do not bear the hole,



but one may also notice the occurrence of effective hopping integrals between non-adjacent atoms



In this process the hole jumps to the second-neighbour atom. Once may notice a similar second-order process which simultaneously changes one hole and permutes the spins of two electrons



This effective Hamiltonian proposed by Gadéa *et al.*[139] for the cations of conjugated molecules is able to give many more eigenvectors of the positive ion than Koopman's theorem. It provides a direct estimate of the spectrum of the positive ion, involving the non-Koopmans states, which appear to occur at quite low energy and are described as two-hole one-particle states in the delocalized MO-CI language.

One may then establish that generalizations of the effective Hamiltonians to non-neutral systems are also possible. It is clear that in that case hole delocalization appears explicitly, while for neutral systems the effective Hamiltonian treated the electron delocalization through effective interatomic exchange operator only, or more generally through bielectronic bicentric effective integrals reflecting the back-and-forth electronic movement coupling neutral VB structures. These effects also appear for the cations, when they do not concern the hole, but first-order delocalization effects are also present.

A general scheme picturing the generalization of Heisenberg Hamiltonians is given in Table I.

E. Numerical Applications in the Search of Configuration-interaction Solutions

One should simply mention briefly the application of the effective Hamiltonian approaches which use them as technical tools to solve numerically complex problems. The uses of partitioning techniques and of quasi-degenerate perturbation theory are especially frequent in solving the configuration-interaction (CI) problem in molecular physics.

In most chemical systems, the SCF single determinant represents a good starting point for the description of the ground-state wavefunction. It has a large overlap with the exact wavefunction in the finite basis set, and is energetically well separated from the 'excited' determinants, obtained by single, double, triple,... substitutions of the ground-state occupied molecular orbitals by virtual MOs above the Fermi level. These conditions make relevant a non-degenerate perturbative approach of the ground-state energy and wavefunction, assuming purely monoelectronic definition of the non-perturbed Hamiltonian (as originally suggested by Moller and Plesset[140]) or taking the diagonal part of the full Hamiltonian as non-perturbed Hamiltonian (a version named[141–143] Epstein–Nesbet according to its former applications).

For excited states of molecules, it rapidly appeared that it was quite

TABLE I
Hierarchy of generalizations of Heisenberg Hamiltonians.

Type of problem	Model space	Neutral systems		Cationic systems	
		Neutral VB determinants		One-hole VB determinants	
		1 e^-/AO	2, 1 or 0 e^-/AO	0, 1 e^-/AO	0, 1, 2 e^-/AO
One half-filled band	1 e^-, 1 AO/centre	Heisenberg Hamiltonian (alkali atoms, π system)		hopping integrals + effective exchange + mixed term (π systems)	
	p e^-, p AO/centre	Heisenberg Hamiltonian ← Bloch, des Cloizeaux ← Schmidt orthog. ← interm. Hamilt.	non-Heisenberg Hamiltonian self-repulsion 4 AO operators		unexplored
Non-half-filled band	1 e^-, p AO/centre	magneto-angular effective Hamilt. (B_n)			
	k e^-, p AO/centre	unexplored	unexplored		
Several bands		impossible	back-and-forth bicentric bielectronic effect. integrals, monocentric monoelectr. and bielectr. integrals tentative explorations		unexplored

TABLE II

Comparison of multi-reference CI schemes; after a preliminary choice of a small zeroth-order space S.

1. Partitioning technique/S	2. Preliminary diagonalization of S	3. QDPT construction of an effective Hamiltonian on S[147]	4. Preliminary diagonalization of S	5. Use of generalized degenerate perturbation theory[34] ('shifted B_k approximation'[154]) with S as model space, avoids most of intruder state problems, good size consistency[a]
+ simplification of the outer space matrix Shavitt[144] non-size-consistent[a]	+ independent perturbations of the eigenvectors CIPSI[66,67] MRDCI[145]	→ intruder states, divergence	+ definition of a smaller multi-configuration model space S[150-152] good convergence properties no intruder states approx. size consistency[a]	
	− artefacts in weakly avoided crossings	→ size consistency problems ($\varepsilon \propto 2N$ for second order)[a] if S is not a complete active space		
	− imperfect size consistency[a] $\varepsilon \propto 2N/3$ for CIPSI $\varepsilon \propto \sqrt{N}$ for MRDCI			

[a]Ref. 155; a correct size consistency would be $\varepsilon \propto N$.

impossible to find a satisfactory single-determinantal zeroth-order description. While the ground-state SCF determinant only interacts with doubly substituted determinants of much higher energy (due to the Brillouin's theorem), a singly excited (with two open shells) SCF configuration interacts with all other singly excited configurations, some of them being almost degenerate. For excited-state problems, it becomes necessary to use multi-configurational zeroth-order descriptions, a goal which is also desirable for some ground-state strongly correlated problems, for instance when some bonds are broken or when the molecule has large diradical character.

Methods have then been built to start multi-configuration (multi-reference) zeroth-order descriptions. The full CI space is first partitioned into a (small) main subspace involving the leading configurations for the descriptions of the states to be studied. Then

1. One may use the partitioning technique as suggested by Shavitt *et al.*[144] 20 years ago. If it was applied strictly the method would require the inversion of a very large matrix (cf. Eq. (8)) and would be as expensive as the direct diagonalization. The large matrix is then supposed to be diagonal and the process reduces to the multiplication of rectangular submatrices. The method has not been used frequently for CI calculations because it is no longer size-consistent at this level of approximation.
2. One may diagonalize first the small main subspace S (which involves all the nearly degenerate configurations, the number of which is usually taken from 20 to 200); if P_S is the projector on the main subspace

$$P_S = \sum_{K=1}^{N} |\phi_K\rangle\langle\phi_K|$$

$$P_S H P_S |\psi^0_{mS}\rangle = E^0_{mS} |\psi^0_{mS}\rangle$$

$$|\psi^0_{mS}\rangle = \sum_{K\in S} C_{mK} |\phi_K\rangle \tag{162}$$

the multi-configurational wavefunctions $|\psi^0_{mS}\rangle$ should no longer be degenerate and might (in principle but *vide infra*) be treated independently. Some of these functions may be perturbed to the second order as in the original CIPSI algorithm[66] by configurations outside of S. Other algorithms, such as the MRDCI (multi-reference double CI) [145] of Buenker and Peyerimhoff or the improved CIPSI algorithm,[67] define a second class of determinants of mean importance and treat their effect variationally (i.e. to infinite order). These determinants are usually between 1000 and 10 000, while the others (in number larger than 10^5 or 10^6) are treated to second order only. These procedures do not lead to effective Hamiltonians and are simply mentioned for comparison and forthcoming discussion.
3. One may use directly the quasi-degenerate perturbation theory, or an iterative algorithm, to solve the Bloch equation, taking the main subspace S

as model space. But this procedure usually faces major intruder state problems, since some of the main configurations in the model space are high in energy (for instance, doubly excited configurations embedded in the continuum, without any spectral meaning, but strongly coupled to the ground or low excited configurations). Some more or less diffuse excited configurations which do not belong to S are lower in energy than these doubly excited configurations and happen to behave as intruder states, making the perturbation expansion divergent. This difficulty cannot be solved by including the intruder states in the model space for two reasons: (i) The enlargement of the model space results in a rapid increase of the computational cost. (ii) The newly introduced configurations generate their own set of intruder states and the series remain divergent. Despite this practical problem (see Robb and Hegarty[146]), Bartlett *et al.*[147] have implemented a second-order Rayleigh–Schrödinger QDPT expansion, which has not received many applications (see however Refs. 148 and 149).

4. Instead of using the QDPT expansion in a model space of single configurations, one may choose a model space of multi-configurational wavefunctions resulting from a preliminary diagonalization of a small subspace.[150–152] The preliminary diagonalization of 200 determinants gives a few physically relevant eigenvectors $|\psi^0_{mS}\rangle$ (the number of which will typically be lower than 10). Let us calls this new subspace S_0

$$P_{S_0} = \sum_{m=1}^{n \simeq 10} |\psi^0_{mS}\rangle\langle\psi^0_{mS}| \tag{163}$$

which will be taken as a model space for the QDPT expansion. The resulting effective Hamiltonian has much smaller size than the effective Hamiltonian built on S (i.e. on N determinants). Owing to the multi-configurational nature of $|\psi^0_{mS}\rangle$, one must generate all the determinants from the N $|\phi_k\rangle$, and the cost of the perturbative expansion is equal to that of a direct expansion in the basis of configurations, but the convergence behaviour is better by far, since one only perturbs the lower eigenvectors of $P_S H P_S$, which are energetically far from the determinants outsides of S. The other eigenvectors of $P_S H P_S$ which do not belong to S_0 are closer in energy, but they are not coupled with the vectors spanning S_0 and do not contribute to the second order.

This procedure had been proposed by Daudey and Malrieu.[150] To second order the diagonal corrections of the effective Hamiltonian are identical to those calculated in the original CIPSI algorithm. The procedure simply consists of adding off-diagonal perturbative corrections between the zeroth-order multi-reference wavefunctions. These off-diagonal terms lead, after diagonalization of the effective Hamiltonian, to mixing of the zeroth-order wavefunctions, this mixing being of perturbative origin.

This mixing has proved to be very important in treating correctly the

weakly avoided crossings in multi-reference CI procedures, as shown by Spiegelmann and Malrieu.[151] The construction of a small-sized effective Hamiltonian is necessary to avoid the artefacts noticed by Bonacic–Koutecky *et al.*[153] in the MRDCI scheme,[153] also present in the CIPSI algorithm.

The procedure now currently used in CIPSI calculations under the label 'CIPSI–Brandow' has also been suggested by Schneider *et al.*[152]

5. Another type of effective Hamiltonian has been proposed by Davidson and coworkers[154] for the practical treatment of CI problems in nearly degenerate cases, under the name 'shifted B_k' approximation (which refers to a version of the partitioning technique proposed by Gershgorn *et al.*[144] and already discussed). To second order the effective Hamiltonian

$$H^{\text{eff}} = P_{S_0} H P_{S_0} + P_{S_0} H Q_0 (E_0 - H_0)^{-1} Q_0 H P_{S_0} \qquad (164)$$

is identical to the usual Rayleigh–Schrödinger second-order QDPT effective Hamiltonian, except for the fact that all denominators are taken from a common zeroth-order energy E_0 (that of the lowest-energy configuration, for instance). This procedure, which may be shown to be size-consistent[155] on typical problems, might *a priori* be viewed as a level shift in the model space. It is more relevant to see it as the second-order expansion of the generalized degenerate perturbation theory recently proposed by Malrieu *et al.*[34] and briefly outfield in Section II.A. This procedure has the only defect of being explicitly energy-dependent. It might be used as well after a preliminary first-order diagonalization of the model space, and a redefinition of a main-model subspace on the lowest eigenvectors, as previously proposed in the CIPSI–Brandow scheme.

A general summary of the main CI techniques proposed for the treatment of excited states in nearly degenerate situations is pictured in Table II, mentioning their advantages and defects.

One should notice that these techniques may be used as well to search the solutions of Heisenberg Hamiltonians when the number of neutral VB determinants (i.e. of spin distributions) becomes too large. Sanchez-Marin *et al.* have recently treated[156] the molecular spectroscopy of large conjugated molecules through a Heisenberg Hamiltonian by truncating the basis of determinants and dressing the matrix through the generalized degenerate perturbation theory.[34] The results are very encouraging.

IV. APPLICATIONS OF SIMULATION TECHNIQUES

The applications presented in this section are limited to a selected choice of pseudo-Hamiltonians that will be determined by the non-empirical simulation method presented in Section II.B. The emphasis will be put more on the methodological aspects than on the results of these methods.

Note that our purpose of rigorous modelling cannot be completely separated from earlier research on semi-empirical or model Hamiltonians. On one side these Hamiltonians could be parametrized by theoretical simulation techniques and on the other some experimental data could also be introduced in the simulation techniques, for example in the characterization of truncated Hamiltonians. Finally it should be emphasized that research on pseudo-Hamiltonians and model Hamiltonians is always guided by some intuitive knowledge of the passive and active constituents of the system (atomic cores, atoms in molecules, functional group,...) and by the assumption of transferability of their potentials and interactions.

A. Pseudopotentials

A reasonable assumption for any chemist is that molecules are made up of fixed cores (the nucleus and the inner electrons) and of chemically active valence electrons moving in the field of these fixed cores (frozen-core approximation). Obviously for accurate investigations in spectroscopy this assumption would fail, for example for alkali or alkaline-rich elements on the left of the periodic table, which possess highly polarizable cores. In the following only fixed atomic cores will be considered.

Pseudopotentials describe the interaction of a valence electron with the core of the atoms. They are known in the literature under various names, such as model potentials, effective core potentials,.... Model potentials are generally parametrized from atomic spectroscopic data whereas effective core potentials and pseudopotentials are most often derived from *ab initio* calculations. There is a huge literature on the subject and several review articles.[157-160] The recent paper by Krauss and Stevens is recommended for an overall survey of the subject with applications and comparisons with all-electron calculations.[159] The recent review paper of Pelissier *et al.* is devoted to transition elements.[160] In the following we shall only review the main characteristics of the determination of atomic pseudopotentials by the *ab initio* simulation techniques of Section II.B.

The total Hamiltonian of an atom can be written in atomic units (a.u.) as

$$H = \sum_{i=1}^{N} (-\tfrac{1}{2}\Delta_i - Z/r_i) + \sum_{i<j} 1/r_{ij}. \tag{165}$$

For an even number of electrons, the Fock operator derived from H is

$$\begin{aligned} F &= -\tfrac{1}{2}\Delta + \sum_c (2J_c - K_c) + \sum_v (2J_v - K_v) \\ &= \sum_c \varepsilon_c |\varphi_c\rangle\langle\varphi_c| + \sum_v \varepsilon_v |\varphi_v\rangle\langle\varphi_v| + \sum_{i^*} \varepsilon_{i^*} |\varphi_{i^*}\rangle\langle\varphi_{i^*}| \end{aligned} \tag{166}$$

where the indices c, v and i^* label the core, valence and the excited levels respectively. J and K are the usual Coulomb and exchange operators.

In a pseudopotential approach, one considers explicitly only the N_v valence electrons. Without considering the fixed core energy, the pseudo-Hamiltonian is assumed to be of the form

$$H^{ps} = \sum_{i=1}^{N_v} [-\tfrac{1}{2}\Delta_i + V^{ps}(i)] + \sum_{i<j}^{N_v} 1/r_{ij} \tag{167}$$

In Eq. (167) the atomic *pseudopotential* is a one-electron operator which takes into account the interaction of a valence electron with the core. At large distance from the nuclei, V^{ps} tends to the Coulomb potential $-z/r$ where z is the net charge of the core of the atom. The valence pseudo-Fock operator takes the form

$$\begin{aligned} F^{ps} &= -\tfrac{1}{2}\Delta + V^{ps} + \sum_v (2J'_v - K'_v) \\ &= \sum_v \varepsilon'_v |\varphi'_v\rangle\langle\varphi'_v| + \sum_{i^*} \varepsilon'_i |\varphi'_{i^*}\rangle\langle\varphi'_{*}| \end{aligned} \tag{168}$$

The valence energies become the lowest. Here ε'_v and φ'_v resemble as much as possible the exact solutions ε_v, φ_v of (166). The determination of V^{ps} in (168) may be achieved by minimizing a reduced distance between F^{ps} and F:

$$\| F^{ps} - F \|_{\text{minimum}} \tag{169}$$

Expressions (81)–(83) can be used by considering

$$P = \sum_v |\varphi_v\rangle\langle\varphi_v| \qquad \text{and} \qquad P' = \sum_v |\varphi'_v\rangle\langle\varphi'_v| \tag{170}$$

The method provides valence orbitals in (168) with internal nodes, which closely resemble the original valence Hartree–Fock orbitals of (166). This method has been developed mainly by Huzinaga and colleagues, who determine atomic pseudopotentials (model potentials in their terminology) of the form[161]

$$V^{ps} = -\frac{z}{r}\left(1 + \sum_i C_i r^{n_i} e^{-\alpha_i r^2}\right) + 2\sum |\varepsilon_c| \cdot |\varphi_c\rangle\langle\varphi_c| \tag{171}$$

The pseudopotential is the sum of a function of r(which depends on parameters C_i, n_i, α_i) and a non-local operator diagonal on the basis set of the core orbitals which shifts the core energies above the valence energies in F^{ps}. The parameters of V^{ps} are determined at best from a condition which is very similar to (169).

The advantage of Huzinaga's approach is that the model structure of the valence orbitals is preserved but the price one has to pay is the use of large basis sets of atomic orbitals which are not drastically reduced with respect to those used in standard all-electron calculations. Another approach to the

problem is to start from *coreless* valence orbitals which can be expanded in a smaller atomic basis of Gaussian functions. For computational reasons, this last approach has been advocated by the majority of authors in the last 10 years. Note that these coreless orbitals, hereafter called pseudo-orbitals, are not defined in a unique way. Their definition is slightly different from one group to another. However, in all cases, they are norm-preserving (in contrast with the early pseudopotential methods in solid-state physics). Outside the core their amplitudes are as close as possible to the exact Hartree–Fock solutions and they also tend smoothly towards zero near the nucleus (Fig. 11). All the information used for determining the pseudopotential is contained in the truncated valence Fock-like operator

$$F^{\mathrm{tr}} = \sum_v \varepsilon_v |\phi_v\rangle\langle\phi_v| \tag{172}$$

The ε_v in (172) are still exact energies of the original Fock operator and the ϕ_v are the *a priori* defined nodeless pseudo-orbitals. Instead of using (169) the pseudo-orbital is now determined by[162,163]

$$\| F^{\mathrm{ps}} - F^{\mathrm{tr}} \|_{\mathrm{minimum}} \tag{173}$$

The distance is given by (85) and the projectors on the model spaces of F^{tr} and H^{ps} are

$$P = \sum_v |\phi_v\rangle\langle\phi_v| \qquad P' = \sum_v |\varphi'_v\rangle\langle\varphi'_v| \tag{174}$$

as where φ'_v is a valence pseudo-orbital obtained by the variational solution of the pseudo-Hamiltonian (168).

For most applications, atomic pseudopotentials are in local, semi-local or non-local form. The simplest local form

$$V^{\mathrm{ps}} = V^{\mathrm{ps}}(r) \tag{175}$$

consists of choosing a simple function of r; it is a too crude approximation for

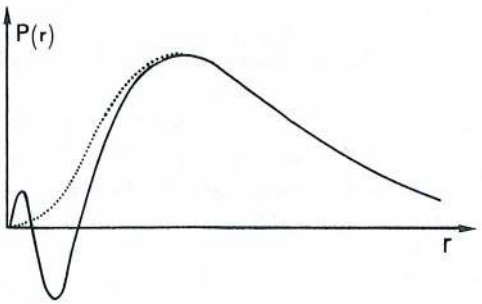


Fig. 11. Radial amplitude $P(r) = R(r) \cdot r$ of a valence Hartree–Fock orbital φ_v (full curve) and of a nodeless pseudo-orbital ϕ_v (dotted curve).

accurate molecular calculations, especially for atoms of the first row of the periodic table. The semi-local form is at the present time the most popular:[164]

$$V^{ps} = \sum_l V_l^{ps}(r) P_l \tag{176}$$

P_l is the projector on the l-space of spherical harmonics. $V_l^{ps}(r)$ is a function of r describing the potential acting on an electron locally of l symmetry. The matrix elements of semi-local pseudopotentials can be expressed in terms of almost analytical expressions, the computational time of which is negligible with respect to that of the two-electron matrix elements. The most general pseudopotentials can be written in the non-local form

$$V^{ps} = -z/r + \sum_{p,q} C_{pq} |f_p\rangle\langle f_q| \tag{177}$$

The functions f_p are generally Gaussian functions. This non-local form is very convenient for molecular calculations which involve the calculation of the overlap between the f_p and the atomic orbitals and for calculation of energy derivation (gradient techniques) for geometry optimizations.

If the Hartree–Fock equations associated with the valence pseudo-Hamiltonian (167) are solved with extended basis sets, then all the above V^{ps} are almost basis-set-independent. At the present time, and for practical reasons, most of the *ab initio* valence-only molecular calculations use coreless pseudo-orbitals. The reliability of this approach is still a matter of discussion. Obviously the nodal structure is important for computing observable quantities such as the diamagnetic susceptibility which implies an operator proportional to $1/r^3$.[165] From the computational point of view, it is always easy to recover the nodal structure of coreless valence pseudo-orbitals by orthogonalizing the valence molecular orbitals to the core orbitals. This procedure has led to very accurate results for several internal observables in comparison with all-electron results. The problem of the shape of the pseudo-orbitals in the core region is also important in relativity. For heavy atoms, the valence electrons possess high instantaneous velocities near the nuclei. Schwarz has recently investigated the compatibility between the internal structure of valence orbitals and the representations of operators such as the spin–orbit which vary as $1/r^3$ near the nucleus.[166]

One should stress the fact that the simulation runs on the ground-state HF solution of the atom only. Despite this fantastic limitation, the method is able to provide reasonable estimates

1. of the correlation energy of this state (slightly overestimated by the nodeless structure of the pseudo-orbital),[167]
2. of the valence multiplet splittings (but *vide infra*),
3. of the Rydberg energies, and
4. of the ionization potentials and electron affinities of the atom,

and of the corresponding energies of molecules involving the pseudo-atom. This success is essentially due to the physically grounded form given to the pseudopotential. The essential defect of this method concerns the lack of core–valence correlation which may be treated later on.

Let us note however that the present methodology of pseudopotentials is based purely on one-electron methods. There is no guarantee with these techniques that the total energies of the various multiplets of an atom will be correctly reproduced from the valence Hamiltonian (167). The problem is particularly difficult for transition elements which involve nearly degenerate configurations, for understanding and computing their properties.[160] Some attempts have already been made to parametrize these pseudopotentials from total energies of the multiplets.[168] Much work remains to be done in this field.

One should also mention discussions concerning the relevant border between the core and the valence shells.[169–172] For copper atom, for instance, one may either consider a ($19e^-$) $3s^23p^63d^{10}4s$, an ($11e^-$) $3d^{10}4s$ or even a ($1e^-$) 4s valence shell. In the latter case the core polarizability effects must be treated explicitly. As an extreme case, one might introduce ($0e^-$) pseudopotentials, for a rare gas for instance, which would be very useful to treat molecular interactions and matrix spectroscopy results. Attempts to define Ar ($0e^-$) pseudopotentials from the virtual MO spectrum of Ar have failed to give relevant intermolecular energies and diatomic extraction appeared to be necessary.[173]

B. Groups and Fragments

Very often the chemical properties of a molecule or of a functional group are governed by a few electrons. For instance, the donor properties and proton affinity of ammonia can be understood from the character of its lone pair; bonding properties of an alkyl radical depend on its unpaired electron. As these molecules or functional groups are basic entities in chemistry, it can be conjectured that they could be described by fragment pseudopotentials quite similar to the atomic pseudopotentials associated with the cores of the atoms.[174]

Such a pseudopotential has been derived by Morokuma *et al.*[175] for ammonia. The 10-electron molecule is reduced to a fictitious system of two active electrons, those of the lone pair moving in the field of the three inactive electron pairs of the N–H bonds. The interaction between the lone pair and the other electrons and the nuclei of the molecule is described by means of a fragment potential (an effective fragment potential according to the terminology of the authors).[175] Their method is a straightforward extension of the techniques developed by Huzinaga. The interest in such an investigation is obviously to obtain transferable fragment potentials. Morokuma *et al.* have

checked that their pseudopotential led to accurate results for predicting bond distances and bond energies when ammonia considered as a fictitious two-electron systems reacted with electron acceptors such as H^+ or BH_3. This is an encouraging result which suggests that determining fragment potentials for CO, PH_3, ... would be very useful in the treatment of coordination chemistry problems. In the following the main steps of the derivation of a fragment potential by simulation techniques is applied to an open-shell one-electron pseudo-atom.

Let us consider a crystal of silicon and suppose that we are interested in a study of the local distortion associated with the creation of a vacancy in the crystal. For such local properties in the vicinity of the vacancy it may be reasonable to simulate the infinite crystal by a finite cluster of atoms. The silicon atoms on the surface of the cluster have to be replaced by one-electron pseudo-atoms denoted Si*. The saturation of a finite cluster by H atoms would be irrelevant since the Si–H bonds are polar and short, inducing artefactual polarization effects in the vacancy region. If the Si–H bonds are lengthened to the Si–Si bond length, the Si–H bond is too weak and introduces artefacts in the monoelectronic energy spectrum. A correct pseudo-atom Si* should bring one electron only, building a non-polar single bond with one Si atom. A convenient monoelectronic pseudopotential describing Si* can be chosen to be of the form

$$V_{\mathrm{Si}^*}^{\mathrm{ps}} = -1/r + \sum_{p,q} C_{pq} |f_p\rangle\langle f_q| \tag{178}$$

The first term in (178) provides a correct asymptotic Coulomb dependence. The second term is a non-local operator of symmetry C_{3v} projected onto a finite basis of functions f_p. The C_{pq} are coefficients that will be best determined by simulation. The theoretical parametrization of (178) can be obtained from a full *ab initio* all-electron calculation on the disilane molecule and on the fictitious system SiH_3Si^*. These two systems contain the relevant information on the Si–Si bond (Fig. 12).

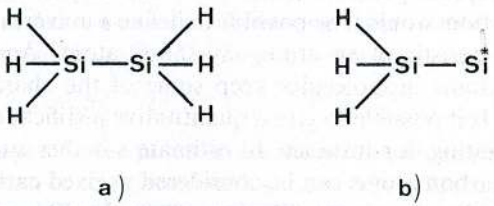


Fig. 12. (a) Disilane (14 valence electrons). (b) Fictitious molecule with a one-electron pseudo-atom of silicon Si* (eight valence electrons).

One can define a truncated Fock Hamiltonian as

$$F^{tr} = PFP = \sum_{p,q=1}^{4} \varepsilon_{pq} |\varphi_p^{loc}\rangle\langle\varphi_q^{loc}| \tag{179}$$

where F is the original Fock operator of the disilane molecule and P is the projector corresponding to the six Si–H bonds and to the Si–Si bond. The localized orbitals φ_p^{loc} are determined by a proper orthogonal transformation of the delocalized Hartree–Fock orbitals. Other definitions of these bond orbitals are possible in close analogy with the definition of the coreless pseudo-orbitals reviewed in Section IV.A. Finally V_{Si*}^{ps} is obtained by minimizing a convenient distance between F^{ps} and F^{tr}. F^{ps} is the Fock pseudo-Hamiltonian arising from the solution of the pseudo-Hamiltonian of SiH_3Si^*.

The same technique could be used for deriving fragment potentials of the alkyl radical to be used for instance in the treatment of alkylated conjugated hydrocarbons. One should note that the pseudo-alkyl group may be a single-electron group, and one will only require σ type AOs in the subsequent molecular treatment if one is only interested in the inductive effect. If one is interested in the hyperconjugative effect too, one should introduce π type AOs on the pseudo-CH_3 and determine a π symmetry potential to mimic the acceptor ability of the σ^* MOs.

C. Atomic Operators for Pseudo-fock Molecular Calculations[45]

Despite their strong limitations, purely monoelectronic pictures, as the Hückel scheme (especially extended Hückel theory) or the tight-binding band model in solid-state physics, support a basic representation of the electronic population. These semi-empirical systematics are supposed to mimic the exact Fock monoelectronic operator, *without* calculating the integrals of the static electronic field and the exchange integrals. It might be tempting to avoid the semi-empirical fitting of parameters and to define a purely monoelectronic molecular operator which would simulate as closely as possible the exact Fock operator. This would ensure better reliability of Hückel-type models, which are so convenient.

From a conceptual point of view, this technical problem is related to a qualitative question: would it be possible to define a universal monoelectronic potential characteristic of an atom, say the C atom? Any chemist would consider that atoms in molecules keep some of the characteristics of the isolated atoms. Is it possible to give a quantitative justification of this idea? It would be interesting, for instance, to estimate whether singly, doubly and triply bonded carbon atoms can be considered as fixed carbon atoms in the series of saturated and conjugated hydrocarbons. It will be shown below that quantum chemistry is able to determine *purely monoelectronic* (pseudo)potentials of atoms in molecules and to check their transferability.

This will be done by the theoretical simulation techniques described in Section II.B by extracting information from molecular *ab initio* all-electron calculations.

Let us consider a molecule made up of atoms A, B, C,.... It is assumed that the Fock operator can be written as the sum of the kinetic energy and of the various atomic potentials in the molecule

$$F^{ps} = -\tfrac{1}{2}\Delta + \sum_{A} V_A^{ps} \tag{180}$$

V_A is the monoelectronic pseudopotential of atom A. (Notice the disappearance of any r^{-1}, J or K operator.) For computational simplicity it may be chosen in the form of a non-local operator:

$$V_A^{ps} = \sum_{p,q} C_{pq} |f_p\rangle\langle f_q| \tag{181}$$

The theoretical determination of the coefficients C_{pq} proceeds as follows. In a first step one determines the valence Fock operator of a molecule containing A. This can be done by solving the valence pseudo-Hamiltonian which leads to

$$F = \sum_{v} \varepsilon_v |\varphi_v\rangle\langle\varphi_v| \tag{182}$$

For economy we intend to perform further molecular calculations within a minimal basis set of atomic orbitals. Then the parametrization of F has to be performed not from F but from the truncated valence Fock operator

$$F^{tr} = \sum_{v} \varepsilon_v |\varphi_v^{appr}\rangle\langle\varphi_v^{appr}| \tag{183}$$

The φ_v are exact Hartree–Fock energies of (182) and the φ_v^{appr} are approximate valence molecular orbitals computed within a minimal basis of Slater orbitals (2s and 2p orbitals for a carbon atom). Finally the determination of the C_{pq} in (181) is obtained by minimizing a reduced distance between F^{ps} and F^{tr}, the trace being kept in the subspace of the φ_v^{appr}. Most often the information contained in one molecule is insufficient to obtain *transferable* potentials. For example, the extraction from CH_4 gives information which is only valid for C–H bonds. To determine universal atomic potentials able to reproduce the formation of single, double and triple carbon–carbon bonds, one needs to extract information from molecules containing these bonds. This has been done by minimizing a distance involving ethane, butadiene and acetylene:

$$(\| F^{ps} - F^{tr} \|_{butane} + \| F^{ps} - F^{tr} \|_{ethylene} + \| F^{ps} - F^{tr} \|_{acetylene})_{minimum} \tag{184}$$

This technique has provided a potential for the carbon atom which is *universal* in the sense that it can be transferred with good accuracy in the whole series of hydrocarbon compounds.[45,176] The main advantage of simulating the Fock operator by the kinetic operator plus the sum of atomic potentials is to produce approximate valence Fock Hamiltonians which can be solved with

computational times similar to those of the Hückel method. Under the (confusing) name of valence effective Hamiltonian (VEH) the method has been widely applied by Brédas *et al.* to band calculations of organic polymers especially for polyacetylene, polyethylene, polythiophene and polypyrole. Useful estimates have been found from these methods concerning ionization potentials, band widths, band gaps and electrical conductivity properties of doped polymers.[177–182]

D. Simulation of Bielectronic Operators

To our knowledge, a rigorous simulation of bielectronic operators has never been attempted. One might use this technique for instance to fit bielectronic integrals. Turning again to the H_2 problem, one might wish to work in a minimal basis set to use exact monoelectronic operators and to reduce the bielectronic integrals to (aa, aa) and (aa, bb), as occurs in CNDO approximations, determining their values to give the best simulation of the lowest states, both the energy *and* the wavefunction. As previously discussed (Section III.C) the valence states which one may reproduce in a minimal basis set are the $(X)(^1\Sigma_g^+)$, $(b)^3\Sigma_u^+$, $(B)^1\Sigma_u^+$ and $(E, F)^1\Sigma_g^+$ states. The wavefunctions of these states should be reduced to their valence components according to Eqs. (135) and renormalized. Since one searches Hermitian operator, the two $^1\Sigma_g^+$ states should be made orthogonal, either by a symmetrical or a Schmidt orthogonalization, the second solution appearing to be preferable to save information. Then the most relevant truncated Hamiltonian would be defined from

$$
\begin{aligned}
{}^1\psi_g &= [(\cos\varphi)(|a\bar{b}| + |b\bar{a}|) + (\sin\varphi)(|a\bar{a}| + |b\bar{b}|)]/\sqrt{2} \\
{}^3\psi_u &= (|a\bar{b}| - |b\bar{a}|)/\sqrt{2} \\
{}^1\psi_u &= (|a\bar{a}| - |b\bar{b}|)/\sqrt{2} \\
{}^1\psi'_g &= [(\sin\varphi)(|a\bar{b}| + |b\bar{a}|) - (\cos\varphi)(|a\bar{a}| + |b\bar{b}|)]/\sqrt{2} \\
H^{tr} &= E((X)^1\Sigma_g)|^1\psi_g\rangle\langle{}^1\psi_g| + E((b)^3\Sigma_u^+)|^3\psi_u\rangle\langle{}^3\psi_u| \\
&\quad + E((B)^1\Sigma_u^+)|^3\psi_u\rangle\langle{}^3\psi_u| + E((E, F)^1\Sigma_g^+)|^1\psi'_g\rangle\langle{}^1\psi'_g|
\end{aligned}
$$

The simulation determining the effective integrals (aa, aa) and (aa, bb) may then concern

1. the ground state only, which involves two degrees of freedom, namely the energy and the angle φ, and implies both (aa, aa) and (aa, bb),
2. the ground state and the triplet state, the latter implying (aa, bb) only,
3. the ground state, the triplet state and the purely ionic singlet state, the latter implying (aa, aa) only, or
4. the four states.

It would be interesting to compare the values of the integrals so obtained,

the reduced distances between H^{ps} and H^{tr}, and the errors on the valence states which were not involved in the simulation process. (This exercise should preferably be performed simultaneously on the mono- and bielectronic pseudo-integrals, in order to avoid a simulation of the hybridization effect (largely monoelectronic) through the bielectronic integrals.)

One should note that some of the difficulties mentioned in Section III.C may be met here, if one wants to simulate too many states. If the simulation concerns only the two neutral states (X) and (b) (solutions 1. and 2.), there is no ambiguity and no continuity problem, but the ionic states may be quite erroneous. If the simulation also concerns the lowest ionic state (solution 3.) there will be a problem in assigning its energy at large interatomic distances, due to the change of the $(B)^1\Sigma_u^+$ state into a Rydberg state. The same trouble occurs even at short interatomic distances for the upper $(E, F)^1\Sigma_g^+$ state, which is no longer valence for $r \simeq r_e$.

A preliminary diabatization, defining valence ionic $^1\Sigma_u^+$ and $^1\Sigma_g^+$ diabatic states, would be necessary before defining H^{tr}, in order to avoid these intruder state problems.

It is interesting to note that the intruder state problem, which appeared explicitly in the effective Hamiltonian approach, is also present in pseudo-Hamiltonian formalisms when the simulation is too ambitious and claims to concern some states strongly mixed with other states out of the model.

V. CONCLUSIONS

Both the methodological part and the review of applications have shown the similarities and differences between effective Hamiltonians and pseudo-Hamiltonians. The similarities sometimes concern the purpose of the modelling (for instance the reduction to a minimal basis set) which may be attained in one way or another. They also concern the use of some *reduction of information* to a definite part (in general the lowest one) of the spectrum. This reduction is explicit in the effective Hamiltonian theory, through the choice of a *model space*, while in the pseudo-Hamiltonian approach it goes through the choice of a *reduced distance* between the exact Hamiltonian and the pseudo-Hamiltonian.

But it must be clear that this reduction of information and this focus on some low part of the spectrum proceed differently and lead to completely different tools. The effective Hamiltonians appear as *N-electron operators* acting in well defined finite bases of N-electron functions. The effective Hamiltonians obtained from the exact bielectronic Hamiltonian introduce three- and four-body interactions. They may essentially be expressed as *numbers* multiplied by products of creation and annihilation operators. In contrast, the pseudo-Hamiltonians keep an *a priori* defined *analytic* form, sometimes simpler than the exact Hamiltonian to mimic. For instance, the

core pseudopotentials are monoelectronic while they simulate complex one- and two-body effects.

As another important difference between the two philosophies one may stress the fact that the effective Hamiltonians acting out of the model space simply give zero, while the pseudo-Hamiltonians give some flexible answer, the reliability of which essentially depends on the physical realism of the pseudo-operators assumed at the beginning of the simulation. The core pseudopotentials are an excellent example of this flexibility; extraction proceeds on the ground (valence) state of the atom, and the resulting pseudopotential is apparently able to give with a good accuracy the various valence multiplets, the Rydberg spectrum, and the positive and negative ion energies, provided that the pseudopotential has a reasonable shape with a short-range repulsive potential and a Z^{eff}/r long-range tail. This flexibility, this ability to follow physical situations which were not involved in the simulation process (since not concerned in the reduced distance), explain the greater success of pseudo-Hamiltonians over the more rigorous but too rigid effective Hamiltonian approaches.

The two methodologies should not be considered as contradictory; they may be used in conjunction, as has been mentioned. It may be useful for instance to use the projection approach, defining a valence effective Hamiltonian, which will be later mimicked (as H^{tr}) by simulation techniques. The diabatization potential energy surfaces might be an important step to define valence states, in regions where non-valence intruder states appear, before simulating them by pseudo-Hamiltonian techniques.

One of the contributions of the present review concerns the question of the intruder state. This question is frequently seen as convergence trouble in a perturbation expansion. Moving back to the basic equations defining the wave operator and the effective Hamiltonian, it appears that the intruder state problem is a problem concerning the *definition of the target space*, when the correspondence between the model space and the target space becomes ambiguous. Two choices have been proposed, based on either a projection criterion or an adiabatic energy following, but both solutions lead to major difficulties if transferability of effective interactions is desired.

One should finally stress the fact that more flexible algorithms should be sought in the field of effective Hamiltonian theory. For a given model space (of dimension $N_m + N_i$) the lowest part of the spectrum involving only N_m roots, for instance, must satisfy the basic properties of effective Hamiltonians (i.e. the roots must be exact energies and projections of exact eigenvectors) while the upper part of the spectrum must simply be realistic, continuously varying with internuclear distance. In simulation techniques this flexibility may be obtained by the weighting coefficients appearing in the reduced distance. In effective Hamiltonian techniques, Gram–Schmidt or hierarchized hermitization of the effective Hamiltonians, which proved to be a fruitful technique, is a step

along this direction, since it favours the lowest part of the spectrum, the eigenvectors of the upper roots deviating significantly from the projections of the exact eigenvectors in the model space. The introduction of intermediate Hamiltonians as a new class of more flexible effective Hamiltonians is inspired by the same philosophy. It consists of accepting, for consistency reasons, to work in a rather large model space, but to lose some accuracy in both the energies and eigenvectors of the upper roots. These techniques, which directly realize some approximate diabatization when intruder states appear, may solve many of the intruder state problems.

Both effective Hamiltonians and pseudo-operators achieve rigorous simplifications of the *ab initio* schemes. They offer a way to recombine the two fundamental tasks of quantum chemistry, namely the desire for numerical accuracy and efficiency and the desire for understanding the forces governing the electronic population.

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