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Origins of the poor convergence of many-body perturbation theory expansions from unrestricted Hartree–Fock zeroth-order descriptions

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Besides unavoidable discontinuities of the finite-order potential curves derivatives at the symmetry-breaking point, the UHF Möller–Plesset perturbation series show very slow convergence at intermediate and large interatomic distances. This bad behavior has two origins: (i) the MP denominators tend towards a constant value instead of vanishing so that each contribution is decreasing too rapidly with the interatomic distance; this remark condemns the use of MP zeroth-order Hamiltonian and forces to adopt an Epstein–Nesbet definition; (ii) the coupling between the singly and doubly excited determinants is very strong at intermediate distances, and the effect of the singly excited configurations, which only appears at the fourth order, slows down the convergence rate. These trends are both analytically demonstrated and numerically illustrated in the model minimal basis sets $He_2^{+ \, +}$ and N_2 problems. A proposal to include the effect of singly excited determinants through a low-dimensional effective intermediate-type Hamiltonian has significantly improved the second-order results. By the way it is demonstrated that the perturbation from a singlet symmetry-broken HF solution (charge instability) necessarily diverges at intermediate distance.

I. INTRODUCTION

The many-body perturbation theory (MBPT)[1] starting from a restricted Hartree–Fock zeroth-order description of the molecular wave function is especially useful for the study of electronic correlation in atoms and molecules. In its Rayleigh–Schrödinger version it leads to the linked cluster theorem,[2] insuring a correct size consistence (i.e., dependence on the number of particles). However, this method faces a major difficulty for the study of potential energy surfaces; it diverges when covalent bonds A–B are broken into radicalar framents $A^{\cdot} + B^{\cdot}$, since for large interatomic distances a (near) degeneracy occurs between the RHF ϕ_0 determinant and some excited determinant. Multideterminantal descriptions are required for the bond-breaking region, and should be considered as zeroth-order descriptions. The use of quasidegenerate perturbation theory[3] is in principle possible, but it is not easy to define a model space which satisfies both a size-consistence requirement and good convergence properties for all internuclear distances; the so-called "complete model spaces" which insure the first property face tremendous intruder state problems at short interatomic distances.[4]

In principle the symmetry-broken unrestricted Hartree–Fock (UHF) single determinants should avoid this contradiction since they correctly dissociate into UHF solutions of the separate atoms; actually, UHF MBPT expansions have been proposed and used[5] in the recent years. However any symmetry-broken HF solution of the type $A(S_z = p/2) \cdot B(S_z = -p/2)$ is degenerate with a left/right inverted solution $A(S_z = -p/2) \cdot B(S_z = p/2)$ which is at least a linear combination of excited determinants from the first solution, and convergence troubles might occur as well. Moreover, a few systematic studies exhibited another difficulty, namely a very slowly convergent behavior; this defect has been noticed by Nyden and Petersson[6] on the H_2 problem, and higher orders corrections have been studied by Handy *et al.*[7] on the H_2O and NH_2 problems and by Gill and Random[8] on the H_2 isoelectronic problem $He_2^{+ \, +}$ in a minimal basis set, where the potential energy barrier remains twice the exact value at the tenth order. Similar difficulties (underestimation of the correlation energy at intermediate distance, typically 0.5 to 2. bohr after the occurrence of symmetry breaking) have been noticed for the F_2 single bond by Laidig *et al.*[9] and by Gordon and Trulhar[10] and for the triply bonded N_2 molecule.[9]

Besides these convergence difficulties it may be shown that all orders ($n > 1$) potential surfaces exhibit an angular behavior at the point where the symmetry breaking occurs.

Moving back to the convergence problem one should notice that most calculations used a Möller–Plesset[1] (MP) definition of the zeroth-order Hamiltonian H_0 (except Ref. 6). The present work shows that MP denominators suffer from a spurious asymptotic trend which slows down the convergence rate; it will be demonstrated both analytically and numerically on the singly bonded $He_2^{+ \, +}$ and triply bonded N_2 systems in minimal basis sets.

An Epstein–Nesbet[11] definition of H_0 avoids this spurious denominator shift but may result in divergent behavior of the series. Moreover the role of single excited determinants, which only appear with the fourth order, is very important, as noticed in Refs. 6 and 8, and cannot be omitted without significant underestimation of the energy at intermediate distances. The present work proposes a procedure—referred to the intermediate effective Hamiltonian theory[12]—to dress the valence double excited states by the singly excited configurations, in order to get more realistic potential energy surfaces.

Most of the demonstrations of the present paper remain on simple deductions from asymptotic behaviors of the UHF solutions between the RHF and the atomic UHF limits. However, a full analytic development of the two-electron two- AOs problem (i.e., the H_2 or $He_2^{+\,+}$ case in a minimal basis set) is given in the Appendix.

II. THE CUSP OF THE FINITE ORDER ENERGY AT THE INSTABILITY POINT

Let us call r_c the internuclear distance where the symmetry-broken solution appears, i.e., from which the UHF solution is lower in energy than the RHF one. Cizek and Paldus[13] have already noticed that

$$\left(\frac{\partial \phi_0^{\mathrm{UHF}}}{\partial \lambda}\right)_{\lambda = \lambda_c^+} \neq \left(\frac{\partial \phi_0^{\mathrm{RHF}}}{\partial \lambda}\right)_{\lambda = \lambda_c^-},$$

where λ is the (U/β) (i.e., correlation/delocalization) ratio. This ratio is a continuous increasing function of the interatomic distance and one may expect that

$$\left(\frac{\partial \phi_0^{\mathrm{UHF}}}{\partial r}\right)_{r = r_c^+} \neq \left(\frac{\partial \phi_0^{\mathrm{RHF}}}{\partial r}\right)_{r = r_c^-}$$

and the direct demonstration for the case of the single bond is given in the Appendix. Then it is easy to demonstrate that ϵ^2 has a discontinuous derivative at r_c. The first-order contribution to the wave function

$$|\Psi_1\rangle = \frac{Q_0}{a} V |\phi_0\rangle$$

with

$$Q_0 = 1 - |\phi_0\rangle\langle\phi_0|, \quad a = (E_0 - H_0), \quad H_0|\phi_0\rangle = E_0|\phi_0\rangle,$$

$$\frac{\partial(Q_0/a)}{\partial r} = -\frac{\partial a}{\partial r}\frac{Q_0}{a^2} - \frac{1}{a}\left|\frac{\partial\phi_0}{\partial r}\right\rangle\langle\phi_0| - \frac{1}{a}|\phi_0\rangle\left\langle\frac{\partial\phi_0}{\partial r}\right|.$$

Then

$$\left|\frac{\partial\Psi_1}{\partial r}\right\rangle = \frac{Q_0}{a} V \left|\frac{\partial\phi_0}{\partial r}\right\rangle - \frac{1}{a}\left|\frac{\partial\phi_0}{\partial r}\right\rangle\langle\phi_0|V|\phi_0\rangle$$
$$- \frac{1}{a}|\phi_0\rangle\left\langle\frac{\partial\phi_0}{\partial r}\right|V|\phi_0\rangle - \frac{\partial a}{\partial r}\frac{Q_0}{a^2}V|\phi_0\rangle + \frac{Q_0}{a}\frac{\partial V}{\partial r}|\phi_0\rangle.$$

$|(\partial\phi_0/\partial r)\rangle$ is a linear combination of singly excited determinants and due to the Brillouin's theorem

$$\left\langle\frac{\partial\phi_0}{\partial r}\middle| V \middle|\phi_0\right\rangle = 0.$$

$\langle\phi_0|V|\phi_0\rangle$ is usually taken to be zero so

$$\left|\frac{\partial\Psi_1}{\partial r}\right\rangle = \frac{Q_0}{a} V \left|\frac{\partial\phi_0}{\partial r}\right\rangle - \left(\frac{\partial a}{\partial r}\frac{Q_0}{a^2}V|\phi_0\rangle - \frac{Q_0}{a}\frac{\partial V}{\partial r}|\phi_0\rangle\right)$$

in which the second term is continuous while the first one is different on the right-hand and the left-hand side of the instability point r_c.

The second-order contribution is

$$\epsilon^2 = \langle\phi_0|V|\Psi_1\rangle.$$

It becomes

$$\frac{\partial\epsilon^2}{\partial r} = \left\langle\frac{\phi_0}{\partial r}\middle| V\frac{Q_0}{a} V|\phi_0\rangle\right.$$

$$+ \left\langle\phi_0\middle| V\frac{Q_0}{a} V\middle|\frac{\partial\phi_0}{\partial r}\right\rangle$$

$$- \phi_0|V\frac{\partial a}{\partial r}\frac{Q_0}{a^2} V|\phi_0\rangle + \langle\phi_0|\frac{\partial V}{\partial r}\frac{Q_0}{a} V|\phi_0\rangle$$

$$+ \langle\phi_0|V\frac{Q_0}{a}\frac{\partial V}{\partial r}|\phi_0\rangle.$$

If the real parts of the first two members are nonzero they add and $(\partial\epsilon^2/\partial r)$ is discontinuous at $r = r_c$.

This argument should be generalized to all orders in a recursive manner, and the continuity of the energy will only be restored at infinite order (if the series converge around r_c).

Most of the perturbative works performed within the UHF formalism disguise this discontinuity (see, however, Ref. 8) which may result in serious difficulties for the determination of spectroscopic constants if r_c is close to the equilibrium distance r_e of the molecule (cf. N_2, Fig. 2).

III. ROLE OF DOUBLY EXCITED DETERMINANTS: SPURIOUS EVOLUTION OF THEIR MP ENERGIES

Let us consider first a single bond problem A–B such as H_2 or $He_2^{+\,+}$. Besides r_c the UHF solution becomes $\phi = |\sigma\bar{\sigma}'|$, where σ (respectively σ') has a larger amplitude on atom A (B, respectively). At infinite distances

$$\sigma \to a \quad \sigma' \to b \quad \text{when } r \to \infty,$$

where a and b are the UHF solutions of the separate atoms (i.e., the exact ones for the two-electron problem). Then ϕ_0 tends towards a neutral asymptote $|a\bar{b}|$, and if h, J, and K are the usual monoelectronic, Coulombic, and exchange operators the Fock operator for α spin orbitals F^α tends to

$$F^\alpha \to h + J_a - K_a + J_b,$$
$$F^\beta \to h + J_b - K_b + J_a.$$

So that the eigenvalues E and E^* of the valence bonding and antibonding MOs:

$$F\sigma = E\sigma,$$
$$F\sigma^* = E^*\sigma^*$$

have the following asymptotes:

$$E \to \langle a|h|a\rangle,$$
$$E^* \to \langle b|h|b\rangle + J_{bb}, \quad \text{when } r \to \infty,$$

where J_{bb} is the bielectronic monocentric repulsion integral. Then the MP energy difference relative to the doubly excited determinant $\phi_D = |\sigma^*\bar{\sigma}'^*|$ is

$$\Delta E^{\mathrm{MP}} = 2(E - E^*)$$

which tends towards $-2J_{bb}$, which is large. Notice that this doubly excited determinant tends towards $\phi_D \to |b\bar{a}|$, i.e., a neutral form which should be degenerate with ϕ_0, since it simply results from ϕ_0 by a spin exchange. Actually the EN energy difference

$$\Delta E^{\mathrm{EN}} = \langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle$$

tends toward 0 when $r \to \infty$. It is clear then that the use of MP denominators results in a large and spurious energy shift which does not prevent the convergence of the perturbation expansion but slows it desperately, the energies going to the exact one by upper values. This behavior has been extensively analyzed on a 2×2 matrix by Cizek et al.[14]

One may expect more realistic energies at the lower orders of the EN expansion, but the question of its convergence arises since the $\langle\phi_0|H|\phi_D\rangle/(\langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle)$ ratio is asymptotically undetermined, both factors are going to zero when r increases since

$$\langle\phi_0|H|\phi_D\rangle = \langle\sigma\sigma'|\frac{1}{r_{12}}|\sigma^*\sigma'^*\rangle \underset{+\infty}{\sim} \langle ab|\frac{1}{r_{12}}|ba\rangle \to 0.$$

The Appendix gives a demonstration for the following property:

$$\forall R, \quad |\langle\phi_0|H|\phi_D\rangle/(\langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle)| < \tfrac{1}{4}$$

so that in the two-electron problem with the CI matrix restricted to the doubly excited determinant, the EN series should converge nicely.

The $He_2^{+\,+}$ problem studied in Ref. 8 has been reexamined using the same basis set in both MP and EN series [cf. Figs. 1(a) and 1(b)]. The MP expansion results [Fig. 1(a)] are identical to those of Gill and Radom and simply appear for comparison; at the tenth order the barrier height is correct and the barrier is correctly located in the EN expansion [cf. Fig. 1(b)] while it was twice too large in the MP expansion. The tenth-order EN correlation energies have a maximum 3% error. For very large distances, only a very small part of the correlation energy has been recovered by the MP expansion (8% at 2.6 bohr) at the 15th order while the EN series have converged.

The poor value of the EN_2 energy can only be explained by the role of the singly excited determinants, as will be shown in Sec. IV; Nyden and Petterson had noticed on the isoelectronic H_2 problem that the variational CI of doubly excited determinants leaves a significant error at intermediate distances.[6]

The defect of the MP denominators is a general feature. One may consider for instance the N_2 triple bond. For the lowest spin instability the UHF ground-state determinant keeps the form (neglecting the lone pair MOs).

$$\phi_0 = |\sigma\bar{\sigma}'x\bar{x}'y\bar{y}'|$$ which tends towards the $N(S_z = 3/2).N(S_z = -3/2)$ product of atomic UHF solutions since

$$\sigma\to z_a, \quad \sigma'\to z_b$$
$$x\to x_a, \quad x'\to x_b \quad \text{when } r\to\infty$$
$$y\to y_a, \quad y'\to y_b$$
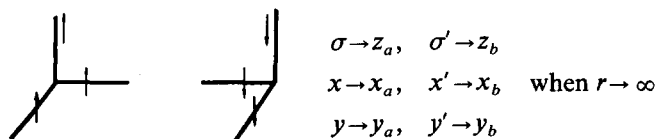
if z is the internuclear axis. The preceding derivation of the asymptotic behavior of the Fock α and β operators may be repeated and it is easy to show that

$$E_\sigma - E_{\sigma^*} \quad \text{tends to} \quad J_{z_a z_a} + K_{z_a x_a} + K_{z_a y_a},$$

i.e., a large value. In that case the doubly excited determinants resulting from spin exchanges in one of the σ or π bonds are no longer degenerate with ϕ_0 at infinite distances:

$$\phi_D\begin{pmatrix}\sigma^*\bar{\sigma}'^* \\ \sigma\ \bar{\sigma}'\end{pmatrix} = |\sigma^*\bar{\sigma}'^*x\bar{x}'y\bar{y}'|$$
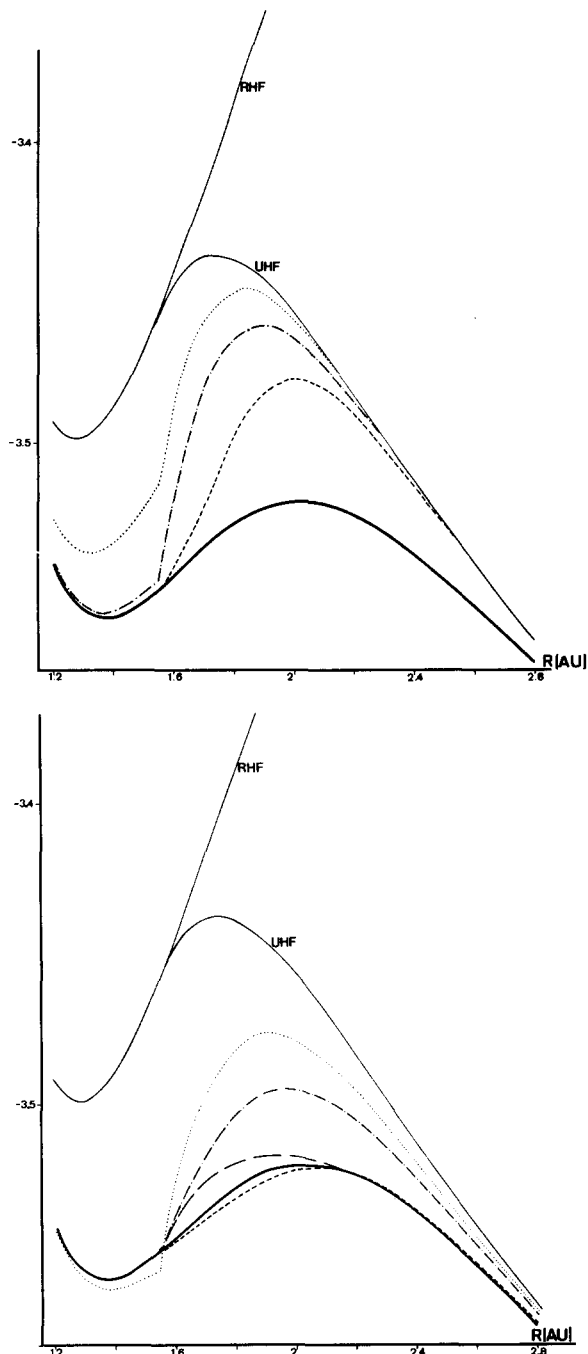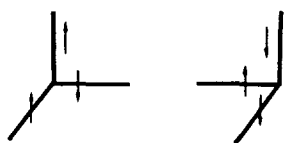

FIG. 1.(a) $He_2^{+\,+}$ in a minimal basis set. The expansion is made with a Möller–Plesset zeroth-order Hamiltonian definition—diagonalization of the CI matrix;—Hartree–Fock zeroth-order energy. The upper curve figures the restricted HF solution and the lower the unrestricted one; ··· second-order UHF energy curve; –·–·–fourth-order UHF energy curve; --- tenth-order UHF energy curve. (b) $He_2^{+\,+}$ in minimal basis set. The expansion is made with an Epstein–Nesbet zeroth-order Hamiltonian definition. Same notations as for (a), plus – – –curve of the second-order energy computed with the intermediate Hamiltonian method (the intermediate model space contains the doubly excited determinant). All energies are expressed in atomic units.

tends towards $|z_b\bar{z}_ax_a\bar{x}_by_a\bar{y}_b|$ is a product $N(S_z = 1/2)\cdot N(S_z = -1/2)$, which is higher in energy than the asymptote of ϕ_0,

$$\langle\phi_D|H|\phi_D\rangle - \langle\phi_0|H|\phi_0\rangle \quad \text{tends to} \quad 4K_{z_a x_a}.$$
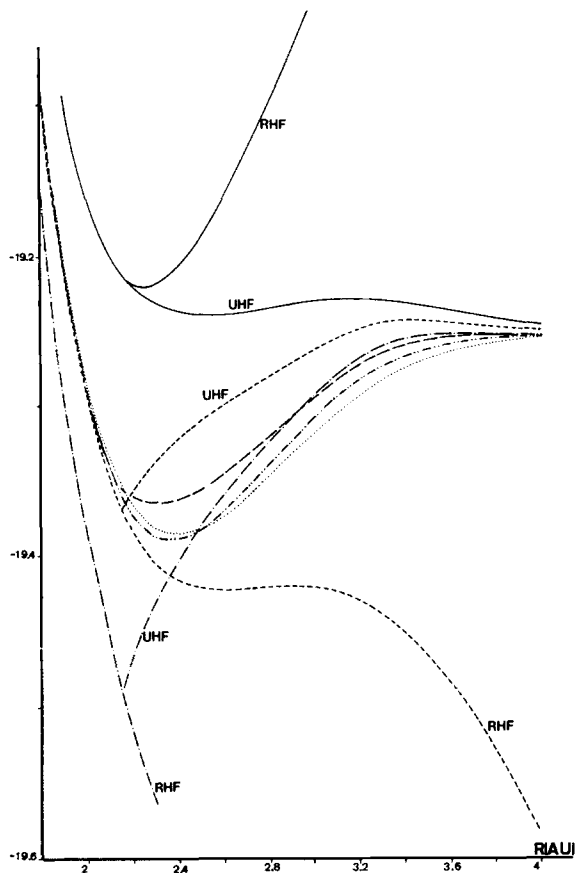
FIG. 2. N_2 in a minimal basis set. $\cdots$ Diagonalization of the CI matrix;— Hartree–Fock zeroth-order energy; the upper curve being the restricted HF solution, the lower the unrestricted HF one;—second-order energy curve, the zeroth-order Hamiltonian being of Möller–Plesset type. (The expansion is made from an UHF zeroth-order wave function for the upper curve and from an RHF one for the lower curve); –·–·–second-order energy curve, the zeroth-order Hamiltonian being of Epstein–Nesbet type. (The expansion is made from an UHF zeroth-order wave function for the upper curve and from an RHF one for the lower curve);—second-order energy curve computed with the intermediate Hamiltonian method, the intermediate model space containing all doubly excited determinants keeping two electrons of opposite spin in each bond;–··–··–second-order energy curve computed with the intermediate Hamiltonian method, the intermediate model space containing all the preceding determinants plus all singly excited ones keeping two electrons in each bond.

While the MP energy difference for such a double excitation is $2(J_{zz} + 2K_{zx})$, the EN energy difference is only $4K_{zx}$, and the MP definition of H_0 again introduces a spurious $-2J_{zz}$ energy shift, leading to a very slow energy convergence. Notice that in that case the excited determinant degenerate with ϕ_0 at long distance is the full spin-exchange sextuply excited determinant.

Numerical calculations have been performed on N_2 using a minimal basis set and are reported in Fig. 2.

Notice first that instability appears for an internuclear distance slightly shorter than the equilibrium one, and that the cusp of the second-order corrected energy is dramatic in that problem. One may notice that MP_2 gives only about 50% of the correlation energy at 2.4–2.8 bohr and becomes even worse at large interatomic distance. MP_4 results are not

much better (they represent 2/3th of the exact correlation energy at $r = 2.4$ bohr). This is in full agreement with the conclusions of Laidig et al.[9] on N_2 in nonminimal basis sets. The errors are less important for these intermediate and long distances when using the EN definition of H_0, but since the EN series diverge close to $r = r_c$, the short-distance EN_2 energies are overestimated.

As a preliminary conclusion one may say that
(i) the MP definition of H_0 cannot be maintained when using UHF MOs;
(ii) the EN expansion is not satisfactory for two reasons, namely the importance of the singly excited configurations, which slows the EN convergence in the He_2^{++} case, and the divergence at short distances for the N_2 problem.
Section IV will analyze the role of the singly excited determinants.

IV. ROLE OF SINGLY EXCITED CONFIGURATIONS

In both problems the singly excited valence determinants ϕ_M are of Σ_u^+ symmetry when using RHF symmetry-adapted MOs and therefore do not contribute to the $X\ ^1\Sigma_g^+$ ground-state energy. Their matrix elements with ϕ_0 are always zero due to the Brillouin's theorem; they can interact with the doubly excited determinants ϕ_D in the UHF region ($r > r_c$) since, for the two-electron problem, for instance,

$$\lambda' = \langle \phi_M | H | \phi_D \rangle = \langle \sigma^* \, \overline{\sigma'} | H | \sigma^* \, \overline{\sigma^{*'}} \rangle$$

$$= \langle \overline{\sigma}\,' | F^\beta + J_\sigma^* - J_\sigma | \overline{\sigma^{*'}} \rangle$$

$$= \langle \overline{\sigma'} | J_{\sigma^*} - J_\sigma | \overline{\sigma^{*'}} \rangle$$

and there is no reason for λ' to be zero for symmetry-broken MOs, but it tends to zero at infinite distances since $|\sigma'\sigma^*|$ leads to $|ba|$ and vanishes everywhere. The matrix element between the singly and doubly excited determinants, which vanishes at $r < r_c$ and $r = \infty$ goes through a maximum value at intermediate distances, as pictured in Fig. 3. For the two-electron minimal basis set problem the CI matrix has the form

$$
\begin{array}{cccc}
\phi_0 & \phi_D & \phi_M & \phi_M'
\end{array}
$$
$$
\begin{bmatrix}
0 & \lambda & 0 & 0 \\
 & -\Delta E & \lambda' & \lambda' \\
 & & -\Delta E' & \lambda \\
 & & & -\Delta E'
\end{bmatrix},
$$

where $\phi_{M'} = |\sigma\overline{\sigma}^*|$, $\langle \phi_0 | H | \phi_0 \rangle$ is taken as zero of energy

$$\lambda = \langle \phi_0 | H | \phi_D \rangle = \langle \sigma\sigma' | \frac{1}{r_{12}} | \sigma^*\sigma'^* \rangle = \langle \sigma\sigma'^* | \frac{1}{r_{12}} | \sigma^*\sigma' \rangle.$$

Notice that ϕ_M and ϕ_M' tend towards ionic limits $|b\overline{b}|$ and $|a\overline{a}|$, respectively. The energy difference between the singly excited and ground-state determinant

$$\langle \phi_0 | H | \phi_0 \rangle - \langle \phi_M | H | \phi_M \rangle = \Delta E'$$

tends to $-J_{bb}$, i.e., towards the limit of $E - E^*$. The MP energy denominators are therefore correct for the singly excited determinants, but are not for the doubly excited ones.
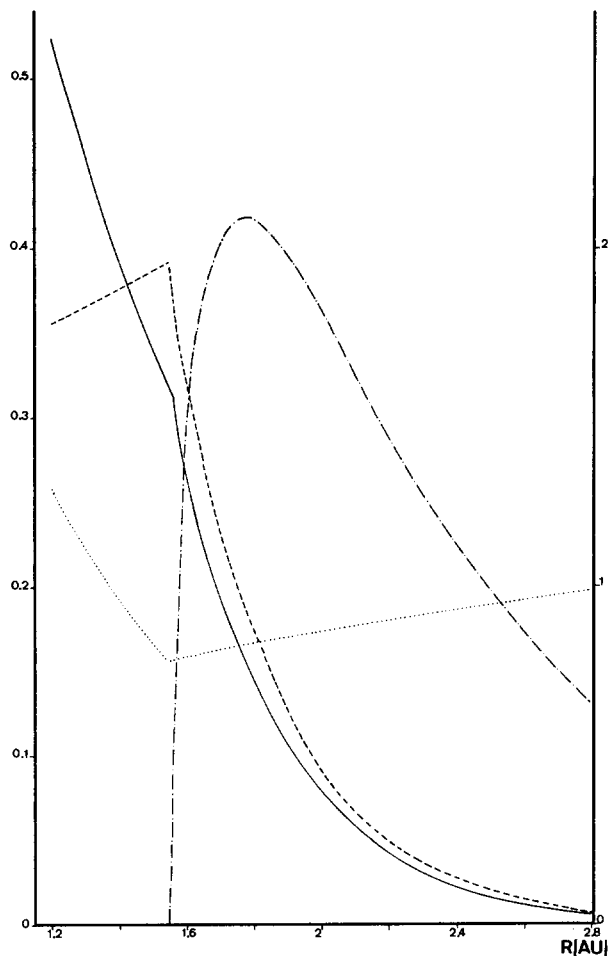
The fourth-order EN correction is

FIG. 3. Matrix elements of the He_2^+ in a minimal basis set problem.--- coupling between the zeroth-order wave function and the doubly excited configuration.-·-·-coupling between the singly and doubly excited configurations. The scale of the two preceding curves is on the left-hand side of the picture;—energy difference between the doubly excited configuration and the zeroth-order wave function;···energy difference between the singly excited configurations and the zeroth-order wave function. The scale of the two preceding curves is on the right-hand side of the picture. Energies are in hartrees.

$$\epsilon^4 = 2\langle\phi_0|V\frac{|\phi_D\rangle\langle\phi_D|}{\Delta E}V\frac{|\phi_M\rangle\langle\phi_M|}{\Delta E'}V\frac{|\phi_D\rangle\langle\phi_D|}{\Delta E}V|\phi_0\rangle$$
$$- \epsilon^2\langle\Psi_1|\Psi_1\rangle.$$

The fourth-order contribution of singly excited determinants is

$$\epsilon_M^4 = 2\frac{h^2}{\Delta E^2}\frac{h'^2}{\Delta E'} = 2\frac{h^2}{\Delta E}\left(\frac{h'^2}{\Delta E\Delta E'}\right) = \epsilon^2\left(\frac{2h'^2}{\Delta E\Delta E'}\right).$$

The ratio $\epsilon_M^4/\epsilon^2 = (2h'^2/\Delta E\Delta E')$ has been pictured in Fig. 4; notice that it tends to 1 when r tend to infinity. This asymptotic behavior is analytically demonstrated in the Appendix.

For intermediate distances the fourth-order contribution of the singly excited configurations is of the same order of magnitude that the second-order effect of the doubly excited determinants.

Since further perturbation orders involve contributions of the type $\phi_0\rightarrow\phi_D\rightarrow(\phi_M\rightarrow\phi_D)^n\rightarrow\phi_0$, these contributions bring an energy
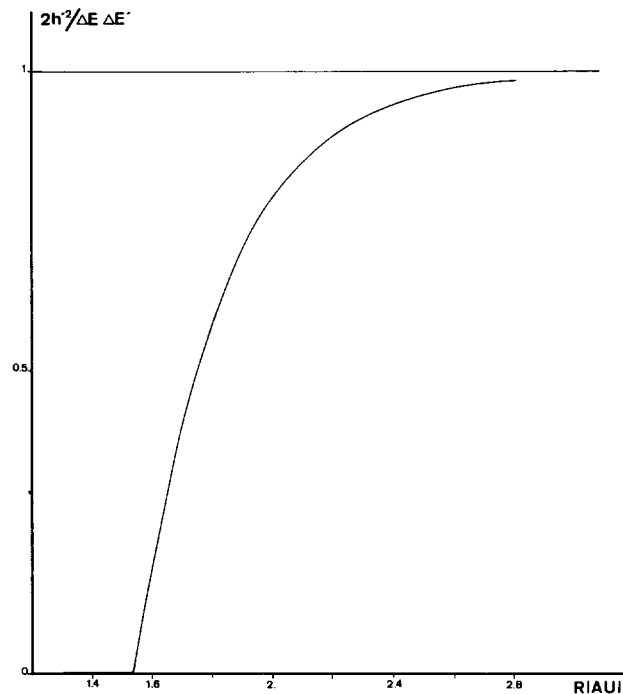

FIG. 4. $He_2^{+ +}$ in a minimal basis set, ratio of the contribution of the singly excited determinants to the fourth-order energy over the second-order energy $(\epsilon_M^4/\epsilon^2 = 2\langle\phi_0|V|\phi_M\rangle^2/\Delta E\Delta E')$.

$$\frac{h^2}{\Delta E}\left(\frac{2h'^2}{\Delta E\Delta E'}\right)^n$$

and $\epsilon^2[1 + \Sigma_n (2h'^2/\Delta E\Delta E')^n]$ is slowly convergent even at intermediate distances. This is the origin of the slow convergence of the EN expansion at intermediate distances.

V. RESEARCH OF PERTURBATION-ADAPTED SYMMETRY-BROKEN MOs

One might have the feeling that the energy minimization of the UHF determinant leads to a too rapid symmetry breaking and that perturbation-adapted symmetry-broken MOs which would go from the molecular RHF into the atomic UHF orbitals in a smoother way have to be searched. A price to pay would be, of course, the loss of the benefit of the Brillouin's theorem, but this is a minor defect if such MOs could be found. Several attempts have been made. One tried to minimize different functionals which seem to be good candidates for measuring the convergence rate. The different functionals which have been tried are

(i) the norm of V (defined either as $\sqrt{\Sigma_{ij}V_{ij}^2}$ or as $\Sigma_{ij}|V_{ij}|$), since one may expect that the smaller the perturbative operator V is, the more rapidly the perturbation series should converge;

(ii) the Kato ratio ($|V|/|$ smallest energy difference$|$) and a functional derived from it $|V|$ $[\Sigma(1/|\Delta E|)]$ because of the importance of the denominators (degeneracy problems);

(iii) the ratio of the fourth-order energy by the second-order one and the functional $|\langle\psi_2|\psi_2\rangle - 1/2\langle\psi_1|\psi_1\rangle^2|$ in order to induce an exponential-like convergence of the series.

TABLE I. Research of perturbation-adapted symmetry-broken MOs for the $He_2^{+\,+}$ problem in a minimal basis set, $R = 1.8$ bohr.[a]

Order α	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\pi/40$	0.1367	−0.0174	−0.0122	0.0078	0.0036	−0.0027	−0.0010	0.0011	0.0003	−0.0005	−0.0001	0.0002	0.0000	−0.0001	0.0000
$2\pi/40$	0.1268	−0.0141	0.0026	0.0128	0.0011	−0.0021	0.0012	0.0006	−0.0009	−0.0003	0.0003	−0.0001	−0.0002	0.0001	0.0000
$3\pi/40$	0.1131	−0.0045	0.0203	0.0152	0.0018	0.0029	0.0023	−0.0007	−0.0004	0.0000	−0.0006	−0.0004	−0.0001	−0.0002	−0.0001
$4\pi/40$	0.0993	0.0124	0.0348	0.0164	0.0083	0.0076	0.0021	0.0006	0.0001	−0.0011	−0.0010	−0.0008	−0.0008	−0.0005	−0.0003
$5\pi/40$	0.0901	0.0348	0.0437	0.0207	0.0166	0.0091	0.0038	0.0015	−0.0011	−0.0017	−0.0021	−0.0021	−0.0017	−0.0014	−0.0009
UHF	0.0887	0.0467		0.0246						−0.0027					−0.0011
$6\pi/40$	0.0904	0.0587	0.0494	0.0292	0.0209	0.0095	0.0042	−0.0011	−0.0034	−0.0047	−0.0049	−0.0043	−0.0034	−0.0022	−0.0012
$7\pi/40$	0.1050	0.0796	0.0564	0.0360	0.0191	0.0060	−0.0033	−0.0090	−0.0115	−0.0115	−0.0096	−0.0067	−0.0033	−0.0001	0.0025
$8\pi/40$	0.1379	0.0936	0.0684	0.0279	0.0082	−0.0190	−0.0259	−0.0343	−0.0268	−0.0193	−0.0039	0.0094	0.0214	0.0282	0.0277
$9\pi/40$	0.1918	0.0972	0.0877	−0.0410	−0.0487	−0.1333	−0.1214	−0.0428	−0.0044	0.2466	0.2599	0.3805	0.2625	−0.2397	−0.4589

[a] Energy error (in atomic units), in an Epstein–Nesbet expansion, from order 0 to 15, for different values of the symmetry-breaking angle α. The RHF symmetry-adapted solution correspond to $\alpha = 0$, $\alpha = \pi/4$ is the totally localized solution ($\phi_0 = |a\bar{b}|$). The value of α corresponding to the UHF solution is about $5.5\pi/40$.

It appears from numerous calculations over all those attempts that none of them is satisfactory; if the MOs are adapted to a specified order of the perturbation series, the further orders are worse and the series diverge or converge slowly in an oscillating way. A confirmation of that bad behavior has been made through a computation of the potential curve of the corrected energies up to the 15th order as a function of the angle α of the symmetry breaking. For the $He_2^{+\,+}$ molecule, the calculations have been made at 1.8 and 2.2 bohr, i.e., just after the symmetry-breaking point, i.e., in the region where the convergence problems are the most dramatic [see Figs. 1(a), 1(b), and 3]. The results are reported in Tables I and II. A careful study of them shows that the only range of α values where the series converges is around the UHF definition of α; outside this range, the series strongly diverge in an oscillating way. Under those circumstances, one should admit that this is not possible to define perturbation-adapted symmetry-broken MOs and so we move back to the UHF MOs.

VI. PROPOSAL OF A LOW DIMENSIONAL EFFECTIVE HAMILTONIAN PROCEDURE

Any procedure starting from UHF MOs must therefore include the effect of the singly excited configurations. A general strategy to include their contribution through a low-order process might consist in building an effective Hamiltonian on the configurations which may become nearly degenerate for some interatomic distances, namely besides ϕ_0 the valence doubly excited determinants which keep two electrons of opposite spins in each bond and dissociate into neutral asymptotes (and eventually valence quadruply or sextuply excited determinants for multiple bonds). From that model space one might think to use the quasidegenerate perturbation theory (QDPT) in one of its versions but since the singly excited determinants are at lower energy than the doubly excited ones at short interatomic distances and far higher at long distances (see also Fig. 3) the $\Delta E - \Delta E'$ energy difference goes through zero at some intermediate distances (near 1.8 bohr in the $He_2^{+\,+}$ problem). Now the second-order QDPT correction to the doubly excited determinant energy is

$$\langle \phi_D | H^{\text{eff}(2)} | \phi_D \rangle = \sum_M \frac{\langle \phi_D | H | \Phi_M \rangle^2}{\Delta E' - \Delta E}$$

and the energy denominator vanishes for some interatomic distances.

The singly excited configurations act as intruder states for the doubly excited determinants and the QDPT expan-

TABLE II. Research of perturbation-adapted symmetry-broken MOs for the $He_2^{+\,+}$ problem in a minimal basis set, $R = 2.2$ bohr.[a]

Order α	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	0.2310	−0.1005	−0.0795	0.1060	0.0700	−0.1400	−0.0764	0.2159	0.0934	−0.3603	−0.1166	0.6330	0.1377	−1.1520	−0.1305
2	0.2100	−0.1132	−0.0405	0.1325	0.0031	−0.1689	0.0689	0.2440	−0.2094	−0.3401	0.5143	0.4245	−1.1465	−0.3576	2.3999
3	0.1783	−0.1113	0.0089	0.1133	−0.0685	−0.0817	0.1713	0.0129	−0.2807	0.1939	0.3537	−0.6167	−0.1821	1.3084	−0.6622
4	0.1403	−0.0899	0.0430	0.0612	−0.0714	0.0225	0.0906	−0.1033	−0.0112	0.1798	−0.1603	−0.1124	0.3886	−0.2232	−0.4185
5	0.1015	−0.0557	0.0527	0.0185	−0.0280	0.0457	0.0041	−0.0323	0.0544	−0.0101	−0.0434	0.0789	−0.0331	−0.0594	0.1275
6	0.0682	−0.0190	0.0453	0.0039	0.0087	0.0239	−0.0049	0.0136	0.0097	−0.0071	0.0154	−0.0024	−0.0037	0.0142	−0.0120
7	0.0461	0.0116	0.0337	0.0101	0.0201	0.0104	0.0092	0.0093	0.0031	0.0059	0.0012	0.0016	0.0010	−0.0013	0.0005
UHF	0.0402	0.0284		0.0186						0.0003					−0.0031
8	0.0406	0.0315	0.0281	0.0202	0.0170	0.0106	0.0082	0.0034	0.0018	−0.0012	−0.0020	−0.0035	−0.0036	−0.0040	−0.0034
9	0.0554	0.0401	0.0332	0.0166	0.0102	−0.0043	−0.0077	−0.0166	−0.0148	−0.0161	−0.0095	−0.0041	0.0042	0.0119	0.0168

[a] Energy error (in atomic units), in an Epstein–Nesbet expansion, from order 0 to 15, for different values of the symmetry-breaking angle α. The RHF symmetry-adapted solution corresponds to $\alpha = 0$, $\alpha = \pi/5$ is the totally localized solution ($\phi_0 = |a\bar{b}|$). The value of α corresponding to the UHF solution is about $7.8\,\pi/40$.

sion has no change to converge at intermediate distances.

An alternative expansion has been recently proposed[12] under the names of generalized degenerate perturbation theory and intermediate Hamiltonians; this theory is based on a partition of the model space into a main model space of dimension m, here restricted to ϕ_0, and an intermediate model space involving here the doubly (and eventually four or six times) excited determinants. The diagonalization of the intermediate Hamiltonian after convergence only delivers m exact roots. In that precise case $m = 1$ and we are only interested in the ground state energy. The main advantage of this formalism is that it avoids any divergence due to a near degeneracy between intermediate vectors and outer intruder states.[15] The second-order corrections are given by[16]

$$\langle \phi_i | \tilde{H}^{(2)} | \phi_j \rangle = \sum_{\substack{\alpha \\ \notin \text{ model space}}} \frac{\langle \phi_i | V | \alpha \rangle \langle \alpha | V | \phi_j \rangle}{E_0 - E_\alpha^0},$$

where E_0 is the energy of the main model space (here ϕ_0). Then the $\Delta E / \Delta E'$ degeneracy in the preceding matrix is no longer a problem. The second-order corrected intermediate Hamiltonian for the two-electron problem is

$$\tilde{H}^{(0+2)} = \begin{matrix} \phi_0 & \phi_D \\ \begin{pmatrix} 0 & h \\ & -\Delta E & +\dfrac{2h'^2}{\Delta E'} \end{pmatrix} \end{matrix}.$$

One may notice that the second-order development of the lowest root gives

$$\epsilon^{(2)} = \frac{h^2}{\Delta E - (2h'^2/\Delta E')},$$

i.e., the infinite summation given above.

Intermediate Hamiltonians have been calculated for both numerical problems (at the second order only) and their lowest solution is given in Figs. 1(b) and 2. For the He_2^{++} problem the order of magnitude of the barrier is now correct (it is overestimated by 10% and it occurs for a slightly too short interatomic distance). The error on the correlation energy reaches about 10% near 1.7 bohr at its maximum (i.e., for the maximum of the λ' matrix element) and the cusp of the potential curve at r_c, although diminished, still remains. For N_2 two intermediate model spaces have been tried. One involves the nine doubly excited determinants which keep two electrons of opposite spins in each bond and which dissociate into neutral asymptotes. In a second calculation the six intrabond single excitations have been added to the previous intermediate space. The results appear in Fig. 2; in both cases the cusp of the potential curve around the instability point almost disappears. When the effect of the valence single excitations is only introduced as a dressing of the energy of doubly excited determinants, the correlation energy remains somewhat underestimated by about 0.7 eV in the region 2.4–3.6 bohr; this defect may be compared with the small extra hump appearing in the He_2^{++} problem for the same level of description. When the valence singly excited states are added to the intermediate space the error is much reduced, peaking at 0.3 eV for $r = 3$ bohr. The general aspect of the potential curve is now quite satisfactory. Notice that it

did not appear to be necessary to introduce in the model space either the quadruply excited spin-exchanging determinants, or the unique valence hexaexcited determinant which tends to become degenerate with the ground-state one at infinite distances. Calculations have actually been performed adding those determinants to the doubly excited ones in the intermediate model space without improving the results significantly.

VII. DIVERGENT BEHAVIOR FOR SINGLET (OR CHARGE) INSTABILITIES

For multiple bonds such as N_2, besides the above discussed triplet instability which leads to the UHF lowest solution of the separated atoms $N(^4S)(s^2syz) + N(^4S)(s^2\bar{x}\bar{y}z)$, it is well known that singlet instabilities take place from a larger critical interatomic distance r_c'.

For such instabilities, the variational single determinant keeps a closed-shell form but the two π MOs are no longer identical,
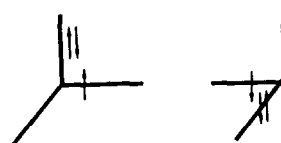
$$\phi_0 = |\sigma_g \bar{\sigma}_g \sigma_u \bar{\sigma}_u \sigma_g' \bar{\sigma}_g' x \bar{x} y \bar{y}|,$$

nor symmetrical with respect to inversion center of the molecule. These π MOs:
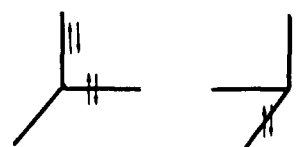
$$x = \alpha x_1 + \beta x_2,$$
$$y = \beta y_1 + \alpha y_2$$

tend to concentrate one on the x_1 AO of the first atom, the other on the y_2 AO of the second atom, so that the asymptote is a linear combination of neutral structures of the type $(s^2 x^2 z) \times (s^2 y^2 z)$:


and of singly ionic structures of the type $(s^2 x^2 z^2) \times (s^2 y^2)$:

This asymptote is far below the RHF symmetry-adapted one which is a democratic mixture of neutral, singly, doubly, and triply ionic structures. At short interatomic distances the $\binom{x \to x^*}{y \to y^*}$ doubly excited determinants are far above ϕ_0, but one may notice that at long interatomic distances the same doubly excited determinants will tend to be spanned by

 or
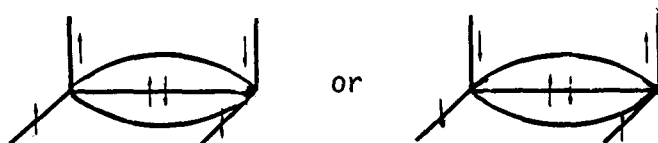
situations (where ↑↓ represents the σ'^2 distribution) and due to the Hund's rule these situations are of lower energy than the
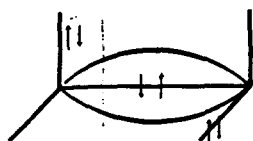
asymptote of the ground state. The doubly excited determinant potential curve therefore crosses somewhere the singlet-UHF ground-state potential curve and the perturbation from that singlet symmetry-broken solution must necessarily diverge in a whole region of interatomic distances (it may converge for long interatomic distances, but would lead in this case to an excited-state energy). It would therefore be hopeless to try a perturbation expansion from singlet instabilities.

VIII. CONCLUSION

The deceptive convergence of usual MB perturbation expansions from a UHF single-determinal solution has two origins:

(i) The first one is the spurious energy shift of the denominators in the Möller–Plesset definition of H_0. Notice that there is no hope in a change of the virtual MOs monoelectronic energies which would insure that $\Delta E^{MP} \to 0$ for doubly excited states as it should, since the singly excited determinants would then become nearly degenerate with ϕ_0 at long distances, while they in fact become purely ionic and well separated in energy. The MP definition, which is so convenient for RHF approaches, seems to be hopeless for UHF zeroth-order descriptions.

(ii) The second origin of this poor convergence is due to the role of the singly excited configurations at intermediate distances; their introduction through a normal single-reference perturbation expansion from ϕ_0^{UHF} is very slowly convergent, even in the EN approach.

A simple procedure has been proposed to deal with their effect by constructing a low-dimensional low-order effective Hamiltonian of the intermediate type. For practical problems, i.e., for nonminimal basis sets, a proper definition of valence virtual MOs would permit to construct valence singly, doubly (and eventually quadruply and sextuply) excited determinants to which the model space may be limited. The set of valence virtual MOs must remain continuous at the symmetry-breaking point; one may, for instance, project the HF AOs of the atom into the molecular virtual space and diagonalize the overlap matrix of these projections to define the most valence virtual MOs, as proposed by Chambaud et al.[17] in a RHF scheme which applies as well in UHF procedures. The process using molecularly defined hybrid atomic orbitals proposed by Illas et al.[18] may also be used. The second-order perturbation on such a small-dimensional model space would remain unexpansive. Nonminimal basis set calculations are explored upon this line.[19] Such procedures may be especially interesting for the treatment of chemical reactions since in the transition state region the UHF solutions are much better than RHF ones and may insure a better continuity of the energy estimates.

APPENDIX: ANALYTIC TREATMENT OF THE MINIMAL BASIS SET SINGLE BOND PROBLEM

1. UHF equations

Let S_a and S_b be the two orthonormalized atomic orbitals, respectively, located on the two atoms referenced as a and b. The RHF MOs are then

$$\sigma = \frac{S_a + S_b}{\sqrt{2}}, \quad \bar{\sigma} = \frac{\bar{S}_a + \bar{S}_b}{\sqrt{2}},$$

$$\sigma^* = \frac{-S_a + S_b}{\sqrt{2}}, \quad \bar{\sigma}^* = \frac{\bar{S}_a - \bar{S}_b}{\sqrt{2}}.$$

Breaking the u–g spin symmetry one may introduce the new MOs:

$$\chi_1 = \cos\alpha S_a + \sin\alpha S_b, \quad \bar{\chi}_2 = \sin\alpha\bar{S}_a + \cos\alpha\bar{S}_b,$$

$$\chi_1^* = -\sin\alpha S_a + \cos\alpha S_b, \quad \bar{\chi}_2^* = \cos\alpha\bar{S}_a - \sin\alpha\bar{S}_b.$$

$\alpha \in [0, \pi/4]$, $\alpha = \pi/4$ corresponds to the RHF MOs, and $\alpha = 0$ corresponds to the atomic orbitals. A new zeroth-order determinant might be defined $\phi_0 = |x_1\bar{x}_2|$, the energy expectation value of which is

$$\langle\phi_0|H|\phi_0\rangle = 2\sin 2\alpha(h_{ab} + \langle a|J_a|b\rangle)$$
$$+ \tfrac{1}{2}\sin^2 2\alpha(J_{aa} - J_{ab}$$
$$+ 2K_{ab}) + J_{ab} + 2h_{aa},$$

where h stands for the monoelectronic part of the Hamiltonian H,

$$J_{aa} = \langle S_a S_a|\frac{1}{r_{12}}|S_a S_a\rangle = (S_a S_a, S_a S_a),$$

$$J_{ab} = \langle S_a S_b|\frac{1}{r_{12}}|S_a S_b\rangle = (S_a S_a, S_b S_b),$$

$$K_{ab} = \langle S_a S_a|\frac{1}{r_{12}}|S_b S_b\rangle = (S_a S_b, S_a S_b),$$

$$h_{ab} = \langle S_a|h|S_b\rangle, \quad h_{aa} = \langle S_a|h|S_a\rangle.$$

The UHF equations are obtained for the value of α which minimizes $\langle\phi_0|H|\phi_0\rangle$, leading to the system

$$\frac{d}{d\alpha}\langle\phi_0|H|\phi_0\rangle = 0 \quad \text{with the constraints}$$

$$\frac{d^2}{d\alpha^2}\langle\phi_0|H|\phi_0\rangle > 0.$$

One has

$$\frac{d}{d\alpha}\langle\phi_0|H|\phi_0\rangle = 2\cos 2\alpha[2(h_{ab} + \langle a|J_a|b\rangle)$$
$$+ \sin 2\alpha(J_{aa} - J_{ab} + 2K_{ab})].$$

The extremas are given by

$$\cos 2\alpha = 0, \quad \alpha = \pi/4 \quad \text{(RHF solution)},$$

$$\sin 2\alpha = -2\frac{h_{ab} + \langle a|J_a|b\rangle}{J_{aa} - J_{ab} + 2K_{ab}}.$$

The second solution exists only if $|f(R)| < 1/2$ where

$$f(R) = \frac{h_{ab} + \langle a|J_a|b\rangle}{J_{aa} - J_{ab} + 2K_{ab}}$$

and R is the interatomic distance. $|f(R)|$ varies as $[e^{-kR}/(k'-1/R)]$ where k and k' are two positive constants so that $\lim_{R\to+\infty}|f(R)| = 0$ and for great R $|f(R)|$ is a decreasing function of R. One might then find a value of R, R_c, for which $|f(R_c)| = 1/2$ and $\forall R > R_c$ $|f(R)| < 1/2$, i.e., the second extrema exists.

Let one now verify that the second derivative is positive for such a solution

$$\frac{d^2\langle\phi_0|H|\phi_0\rangle}{d\alpha^2}\bigg|_{\sin 2\alpha = -2f(R)}$$
$$= 4(J_{aa} + 2K_{ab} - J_{ab})(1 - \sin^2 2\alpha)$$

which is positive for all $R > R_c$:

$$\langle\phi_0|H|\phi_0\rangle|_{\alpha=\pi/4}$$
$$= (2h_{aa} + J_{ab}) + 2h_{ab}$$
$$+ 2\langle a|J_a|b\rangle + 1/2(J_{aa} - J_{ab} + 2K_{ab})$$

and

$$\langle\phi_0|H|\phi_0\rangle|_{\sin 2\alpha = -2f(R)}$$
$$= 2h_{aa} - 2f(R)(h_{ab} + \langle a|J_a|b\rangle).$$

As

$$|\langle\phi_0|H|\phi_0\rangle|_{\alpha=\pi/4} > (2h_{aa} + J_{ab}) - \tfrac{1}{2}(J_{aa} + 2K_{ab} - J_{ab})$$

and

$$\langle\phi_0|H|\phi_0\rangle|_{\sin 2\alpha = -f(R)}$$
$$< (2h_{aa} + J_{ab}) - (J_{aa} + 2K_{ab} - J_{ab}),$$

it becomes that for $R < R_c$, the RHF solution is the unique minimum of $\langle\phi_0|H|\phi_0\rangle$ and for $R > R_c$ there are two minima; the RHF one which is local and the absolute one (unrestricted Hartree–Fock solution) which occurs for $\alpha(R) = \tfrac{1}{2}\arcsin[-2f(R)]$.

2. Discontinuity of the ϕ_0 derivative

The zeroth-order wave function derived from the UHF formalism exhibits a cusp at $R = R_c$.
For $R < R_c$,

$$\phi_0 = |\chi_1\bar\chi_2| = \tfrac{1}{2}(|S_a\bar S_a| + |S_b\bar S_b| + |S_a\bar S_b| + |S_b\bar S_a|).$$

Then

$$\frac{d\phi_0}{dR} = \frac{1}{2}\left(\frac{d|S_a\bar S_a|}{dR} + \frac{d|S_b\bar S_b|}{dR}\right.$$
$$\left. + \frac{d|S_a\bar S_b|}{dR} + \frac{d|S_b\bar S_a|}{dR}\right).$$

For $R > R_c$,

$$\phi_0 = |\chi_1\bar\chi_2| = \frac{\sin[2\alpha(R)]}{2}(|S_a\bar S_a| + |S_b\bar S_b|)$$
$$+ \sin^2[\alpha(R)]|S_b\bar S_a|$$
$$+ \cos^2[\alpha(R)]|S_a\bar S_b|,$$

so that

$$\frac{d\phi_0}{dR} = \cos[2\alpha(R)]\frac{d\alpha}{dR}(|S_a\bar S_a| + |S_b\bar S_b|)$$

$$+ \sin[2\alpha(R)]\frac{d\alpha}{dR}(|S_b\bar S_a| - |S_a\bar S_b|)$$

$$+ \tfrac{1}{2}\sin[2\alpha(R)]\left(\frac{d|S_a\bar S_a|}{dR} + \frac{d|S_b\bar S_b|}{dR}\right)$$

$$+ \sin^2[\alpha(R)]\frac{d|S_b\bar S_a|}{dR} + \cos^2[\alpha(R)]\frac{d|S_a\bar S_b|}{dR}.$$

It becomes

$$\frac{d\phi_0}{dR}\bigg|_{R=R_c^-} = \frac{1}{2}\left[\frac{d|S_a\bar S_a|}{dR}\bigg|_{R=R_c}\right.$$
$$+ \frac{d|S_b\bar S_b|}{dR}\bigg|_{R=R_c} + \frac{d|S_a\bar S_b|}{dR}\bigg|_{R=R_c}$$
$$\left. + \frac{d|S_b\bar S_a|}{dR}\bigg|_{R=R_c}\right]$$

and

$$\frac{d\phi_0}{dR}\bigg|_{R=R_c^+} = \frac{d\phi_0}{dR}\bigg|_{R=R_c^-}$$
$$+ \frac{d\alpha}{dR}\bigg|_{R=R_c}(|S_b\bar S_a| - |S_a\bar S_b|).$$

$$\frac{d\alpha}{dR} = \frac{f'(R)}{\sqrt{1 - 4f^2(R)}}$$

is nonequal to zero for $R = R_c$,
so that

$$\frac{d\phi_0}{dR}\bigg|_{R=R_c^+} \neq \frac{d\phi_0}{dR}\bigg|_{R=R_c^-}.$$

3. Convergence of the EN series

One would like now to demonstrate the property

$$\forall R > R_c,$$
$$\frac{\langle\phi_0(R)|H|\phi_D(R)\rangle}{\langle\phi_0(R)|H|\phi_0(R)\rangle - \langle\phi_D(R)|H|\phi_D(R)\rangle} < \frac{1}{4},$$

where $\phi_D = |\chi_1^*\bar\chi_2^*|$.
One has

$$\langle\phi_0|H|\phi_0\rangle = 2\sin[2\alpha(R)](h_{ab} + \langle a|J_a|b\rangle)$$
$$+ \tfrac{1}{2}\sin^2[2\alpha(R)](J_{aa} - J_{ab} + 2K_{ab}) + J_{ab} + 2h_{aa}$$

and

$$\langle\phi_D|H|\phi_D\rangle = -2\sin[2\alpha(R)](h_{ab} + \langle a|J_a|b\rangle)$$
$$+ \tfrac{1}{2}\sin^2[2\alpha(R)](J_{aa} - J_{ab} + 2K_{ab}) + J_{ab} + 2h_{aa}$$

it becomes

$$\langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle$$
$$= -\Delta E = 4\sin[2\alpha(R)](h_{ab} + \langle a|J_a|b\rangle)$$

$$\Delta E = \frac{8(h_{ab} + \langle a|J_a|b\rangle)^2}{J_{aa} - J_{ab} + 2K_{ab}} \quad \text{for } R > R_c.$$

On the other hand, the coupling is

$$\langle\phi_0|H|\phi_D\rangle = \tfrac{1}{2}\sin^2 2\alpha(J_{aa} - J_{ab} + 2K_{ab}) - K_{ab}$$

$$= \frac{2(h_{ab} + \langle a|J_a|b\rangle)^2}{J_{aa} - J_{ab} + 2K_{ab}} - K_{ab},$$

so that

$$\frac{\langle\phi_0|H|\phi_D\rangle}{\langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle} = \frac{1}{4} - \frac{K_{ab}(J_{aa} - J_{ab} + 2K_{ab})}{8(h_{ab} + \langle a|J_a|b\rangle)^2}$$

$$= \frac{1}{4} - \frac{u(R)}{8}.$$

One might notice that $\forall R$, $u(R) > 0$, i.e.,

$$\frac{1}{4} - \frac{u(R)}{8} < \frac{1}{4}$$

and that for $R = R_c$,

$$\frac{1}{4} - \frac{u(R)}{8} = \frac{1}{4} - \frac{1}{2}\frac{K_{ab}}{J_{aa} - J_{ab} + 2K_{ab}}$$

which is always positive since $\forall R$, $J_{aa} - J_{ab} > 0$.

One would like to prove that for all R:

$$0 < \frac{1}{4} - \frac{u(R)}{8} < \frac{1}{4},$$

it has already been shown that this property is true for $R = R_c$.

Let one make the hypothesis that $\exists R_0$ such that $u(R_0) = 2$, i.e., $\langle\phi_0|H|\phi_D\rangle = 0$, i.e., $|\chi_1\bar{\chi}_2|$ is an eigenfunction of the Hamiltonian.

Case (1), the eigenspace associated with $|\chi_1\bar{\chi}_2|$ is of dimension 1. Then as $[H,S^2] = 0$ (S^2 being the square value of the spin operator), $|\chi_1\bar{\chi}_2|$ is also an eigenfunction of S^2 which is known to be wrong.

Case (2), the eigenspace ζ of H associated with $|\chi_1\bar{\chi}_2|$ is of dimension greater than 1. One knows that $\langle\phi_0|S^2|\phi_0\rangle\in]0,1[$ which means that the unique triplet state T involved in the decomposition of ϕ_0,

$$\langle\phi_0|H|\phi_0\rangle = \frac{\sin 2\alpha}{2}(|S_a\overline{S}_a| + |S_b\overline{S}_b|)$$

$$+ \tfrac{1}{2}(|S_a\overline{S}_b| + |S_b\overline{S}_a|)$$

$$+ \tfrac{1}{2}\cos 2\alpha(|S_a\overline{S}_b| - |S_b\overline{S}_a|),$$

belongs to ζ ($[H,S^2] = 0$ implies that H and S^2 have the same eigenspace) and then have the same energy as ϕ_D. However,

$$\langle T|H|T\rangle = \left\langle\frac{|S_a\overline{S}_b| - |S_b\overline{S}_a|}{\sqrt{2}}\middle|H\middle|\frac{|S_a\overline{S}_b| - |S_b\overline{S}_a|}{\sqrt{2}}\right\rangle$$

$$= 2h_{aa} + J_{ab} + K_{ab},$$

so that

$$\langle T|H|T\rangle - \langle\phi_0|H|\phi_0\rangle$$

$$= \frac{2(h_{ab} + \langle a|J_a|b\rangle)^2}{J_{aa} - J_{ab} + 2K_{ab}} + K_{ab} > 0.$$

One can then conclude that there does not exist any R for which $u(R) = 2$. As u is a continuous function of R and $u(R_c) < 2$ one might insure that $\forall R\, u(R) < 2$ so that $\forall R > R_c$,

$$\left|\frac{\langle\phi_0|H|\phi_D\rangle}{\langle\phi_0|H|\phi_0\rangle - \langle\phi_D|H|\phi_D\rangle}\right| < \frac{1}{4}.$$

4. $2h'^2/\Delta E\Delta E'$ tends towards one when the interatomic distance tends to infinity

Deriving the expressions of the coupling λ' between the monoexcited and doubly excited determinants one should find

$$\lambda' = \langle\chi_1^*\bar{\chi}_2|H|\chi_1^*\bar{\chi}_2^*\rangle$$

$$= -\tfrac{1}{2}\sin 2\alpha\cos 2\alpha(J_{aa} - J_{ab} + 2K_{ab})$$

$$+ \cos 2\alpha(h_{ab} + \langle a|J_a|b\rangle),$$

$$-\Delta E = 4\sin 2\alpha(h_{ab} + \langle a|J_a|b\rangle),$$

$$-\Delta E' = J_{ab} - J_{aa}.$$

So the relative contribution

$$\frac{2h'^2}{\Delta E\Delta E'} = \frac{\epsilon_M^4}{\epsilon^2}$$

of the singly excited determinants is

$$\frac{2h'^2}{\Delta E\Delta E'} = -\frac{1}{8}\frac{\cos^2 2\alpha[\sin 2\alpha(J_{aa} - J_{ab} + 2K_{ab}) - 2(h_{ab} + \langle a|J_a|b\rangle)^2]}{(J_{aa} - J_{ab})(h_{ab} + \langle a|J_a|b\rangle)\sin 2\alpha}$$

which becomes for $R > R_c$, i.e., $\sin 2\alpha = -2f(R)$:

$$\frac{2h'^2}{\Delta E\Delta E'} = \cos 2\alpha\frac{J_{aa} - J_{ab} + 2K_{ab}}{J_{aa} - J_{ab}}.$$

As α tends to 0 when R is going to infinity and

$$\frac{J_{aa} - J_{ab} + 2K_{ab}}{J_{aa} - J_{ab}}$$

tends to 1,

$$\frac{2h'^2}{\Delta E\Delta E'}$$

is going to one when the interatomic distance increases.

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[19]It would especially be interesting to examine their efficiency on the famous Cr_2 problem; previous multireference calculations from UHF MOs by one of us (M.P.) had given a weak attractive well at short interatomic distance (in contrast with other purely *ab initio* attempts from RHF MOs), but with a far too small depth ($\simeq 0.2$ eV) and a spurious hump at larger interatomic distances.