

Perturbation Theory of Intermolecular Interactions: What Is the Problem, Are There Solutions?

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Abstract

We review the nature of the problem in the framework of Rayleigh–Schrodinger perturbation theory (the polarization approximation) considering explicitly two examples: the interaction of two hydrogen atoms and the interaction of Li with H. We show, in agreement with the work of Claverie and of Morgan and Simon, that the LiH problem is dramatically different from the H₂ problem. In particular, the physical states of LiH are higher in energy than an infinite number of discrete, unphysical states and they are buried in a continuum of unbound, unphysical states, which starts well below the lowest physical state. Claverie has shown that the perturbation expansion, under these circumstances, is likely to converge to an unphysical state of lower energy than the physical ground state, if it converges at all. We review, also, the application of two classes of exchange perturbation theory to LiH and larger systems. We show that the spectra of three Eisenschitz–London (EL) class, exchange perturbation theories have no continuum of unphysical states overlaying the physical states and no discrete, unphysical states below the lowest physical state. In contrast, the spectra of two Hirschfelder–Silbey class theories differ hardly at all from that found with the polarization approximation. Not one of the EL class of perturbation theories, however, eliminates all of the discrete unphysical states. The best one establishes a one-to-one correspondence between the lowest energy states of the unperturbed and perturbed Hamiltonians, and a one-to-two correspondence for the higher states. We suggest that the EL class perturbation theories would be good starting points for the development of more effective perturbation theories for intermolecular interactions.

Introduction

Interatomic and intermolecular interaction energies are less easily calculated as small corrections to atomic or molecular energies than as total energies from which the atomic or molecular energies are subtracted. This is contrary to our experience in other areas of science, which raises a question: What makes this problem so different? It is well known that there is an exchange symmetry problem created by dividing the electrons among the interacting atoms and molecules [1–7]. But knowing this has not enabled us to single out one or two of the many proposed perturbation theories as fundamentally better than all the others. Perhaps it is because we have not looked closely enough at the basic problem. In this paper we examine the strength of the perturbing potentials that appear in selected perturbation theories and find that there are enormous differences between them. Based on this criterion, we find that there is no fully satisfactory theory, but that one class of theories may be a good basis for further development.

In part this paper is a review of exchange perturbation theory (EPT) from an unusual perspective. Because a number of fine reviews of the subject have appeared

[1–7], there is no reason for us to attempt a broad, balanced review of what has been done. Indeed, we regard our paper as complementary to Klein's [7]. He has emphasized degeneracy, we emphasize the strength of the interactions as measured by the disparity between the spectra of the unperturbed and perturbed problems. We show that the disparity is gross for certain EPTs, modest for others.

From the work of Claverie [8] and Morgan and Simon [9] it is clear that intermolecular interactions are very strong, not weak. Claverie was the first to point out that there are discrete, unphysical states of lower energy than the physical ground state of a molecule, and that a Rayleigh–Schrödinger perturbation expansion is as likely to converge to one of these unphysical states as to a physical one. Morgan and Simon have simply remarked that in systems containing atoms other than hydrogen and helium, even the lowest energy physical states are buried in a continuum of unbound, unphysical states. These observations are true at infinite as well as finite nuclear separations. Since the unphysical states are not in the spectrum of the unperturbed problem, the perturbation must be very strong.

The idea that intermolecular interactions are weak and, therefore, that interaction energies might be calculated by perturbation methods, probably has its origin in the observation that the dissociation energies of most molecules are very small compared to their total electronic energies. By increasing the distance between atoms in a system, one can reduce the interaction energy until it becomes vanishingly small compared to the total electronic energy. One ought to be able to use for the zero-order Hamiltonian the sum of the atomic Hamiltonians, and for the perturbing potential, the difference between the molecular Hamiltonian and the zero-order Hamiltonian [10]. But these arguments are based on what we know about the physical electronic states of molecules, i.e., states described by totally antisymmetric wave functions. The message of Claverie [8] and Morgan and Simon [9] is that we cannot ignore the unphysical states. Although Eisenschitz and London [11] did not explicitly consider the unphysical states, they effectively did something about them by taking electron indistinguishability into consideration in their perturbation theory. This is the case, also, with the EPTs proposed in the '60s and later. Our objective is to determine how effectively the various EPTs have dealt with the unphysical states.

At this point we must note that in spite of the unphysical states, the Rayleigh–Schrödinger perturbation method can be used to calculate the coefficients in the asymptotic expansion of intermolecular interaction energies in powers of $1/R$, where R is the nuclear separation. This was first proved by Ahlrichs [12]. Morgan and Simon [9] later gave an independent proof, but pointed out that Ahlrichs proof, unlike theirs, was valid even when the state of interest lay in a continuum of unphysical states. But this tells us nothing about the exchange interactions which are so important at intermediate and small R .

We must note, also, that it has been possible to determine the large R asymptotic behaviour of the exchange energy for H_2 [13] and H_3 [14]. Herring and Flicker showed for H_2 that the exchange energy was proportional to $R^{5/2}e^{-2R}$. Shipsey found an exponential dependence for H_3 , too. The method used to obtain these results does not appear to be generally practical.

In the next section we outline the simplest perturbation theory for intermolecular interactions, the polarization approximation. It is essentially the Rayleigh–Schrödinger theory applied to two or more interacting atoms or molecules. We review why electron indistinguishability is a problem, and then derive the spectra of the unperturbed and perturbed problems for H_2 and LiH. The H_2 spectra are simple. The LiH spectra exhibit all of the complications which Claverie and Morgan and Simon found. It will be clear from our discussion that the spectrum of LiH is representative of that of larger molecules. This suggests that numerical tests of perturbation theories, to be realistic, must be done on systems containing atoms with atomic numbers greater than 2.

In the third and fourth sections we derive the spectra of several *effective* Hamiltonians, operators on which EPTs have been based. Those considered in the third section do not have discrete, unphysical states below the lowest energy physical states, nor are the physical states buried in an unphysical continuum. Unfortunately, these Hamiltonians do not succeed in establishing a one-to-one mapping of the physical states onto the unperturbed states. The Hamiltonians considered in the fourth section have almost no effect on the troublesome unphysical states. The fifth section is primarily about what we have and have not done in this paper.

The Polarization Approximation and the Energy Spectrum

We begin with a brief review of the polarization approximation [15], which is basically Rayleigh–Schrödinger perturbation theory applied to the interaction between atoms or molecules. We emphasize the way in which unphysical states may enter into the perturbation expansions. We then derive the spectra of the perturbed and unperturbed Hamiltonians for H_2 and LiH. The derivation for H_2 serves as an introduction to the derivation for LiH. The emphasis in both cases is on using symmetry to lift degeneracies and on locating the unphysical states. Our analysis for LiH supplies the details not provided by Morgan and Simon [9]. It should be clear from our analysis that the situation will be the same for more complicated systems.

The Polarization Approximation and Unphysical States

Let \hat{H} be the Hamiltonian of a diatomic system in the nonrelativistic, Born–Oppenheimer approximation. We write

$$\hat{H}\Phi_k = E_k\Phi_k, \quad \text{where} \quad E_k \leq E_{k+1} \quad (1)$$

and Φ_k denotes a physical eigenfunction of \hat{H} , a fully antisymmetric function of the N -electron position and spin coordinates. In addition to physical eigenfunctions, \hat{H} has unphysical eigenfunctions u_k which vanish when the totally antisymmetric projection operator $\hat{\mathcal{A}}$ is applied. The unphysical states are important to our analysis.

In the polarization approximation for the interaction between two atoms, A and B, one arbitrarily assigns electrons 1 through N_A to atom A, and $N_A + 1$ through $N = N_A + N_B$ to B. Let \hat{h}_A be the Hamiltonian for atom A in the absence of B. It

operates only on the electronic coordinates assigned to A. The customary choice for the unperturbed Hamiltonian is $\hat{H}^0 = \hat{h}_A + \hat{h}_B$. The interaction potential between the two atoms is $\hat{V} = \hat{H} - \hat{H}^0$. Let ϕ_A and ϕ_B be discrete energy, physical eigenfunctions of \hat{h}_A and \hat{h}_B , respectively, and let ε_A and ε_B be the respective eigenvalues. One solution to $\hat{H}^0\Psi^{(0)} = E^{(0)}\Psi^{(0)}$ is $\Psi^{(0)} = \phi_A\phi_B$ with $E^{(0)} = \varepsilon_A + \varepsilon_B$. Bear in mind that $\Psi^{(0)}$ will be antisymmetric under the interchange of a pair of electron position-spin coordinates only if both belong to atom A or both belong to B, but that it will generally have no symmetry for an interchange of coordinates between A and B.

The basic assumption of the polarization approximation is that $\Psi(\lambda)$ exists such that

$$(\hat{H}^0 + \lambda\hat{V})\Psi(\lambda) = E(\lambda)\Psi(\lambda), \quad (2)$$

where

$$\Psi(\lambda) = \sum_{n=0} \lambda^n \Psi^{(n)} \quad \text{and} \quad E(\lambda) = \sum_{n=0} \lambda^n E^{(n)}, \quad (3)$$

and it is required that

$$\langle \Psi^{(0)} | \Psi^{(n)} \rangle = 0 \quad \text{for} \quad n = 1, 2, \dots \quad (4)$$

The expansion parameter λ smoothly links $\Psi^{(0)}$ to $\Psi(\lambda = 1)$, which must be an eigenfunction of $\hat{H} = \hat{H}^0 + \hat{V}$ if the series converges in some sense. One expects the polarization approximation to converge when the perturbation \hat{V} is "weak."

Equations (2)–(4) give rise to the familiar set of equations which determine the n th order function and energy, $\Psi^{(n)}$ and $E^{(n)}$, from the lower-order functions and energies, e.g., $E^{(1)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle$ and $(\hat{H}^0 - E^{(0)})\Psi^{(1)} = (E^{(1)} - \hat{V})\Psi^{(0)}$. Note that from the chosen $\Psi^{(0)}$ one can determine only one $\Psi^{(1)}$ and one $E^{(1)}$. This is true for higher orders, too, although Jeziorski et al. [15] have shown how one may work around this problem.

It was pointed out by Claverie [8] that if the polarization approximation converges for the system, the eigenfunction of \hat{H} that is obtained by solving the set of equations (2)–(4) and going to the limit $\lambda = 1$ may be one of the u_k . One can understand how this occurs by recalling that \hat{H}^0 , $\hat{H}^0 + \lambda\hat{V}$ with $\lambda < 1$, and $\Psi^{(0)}$ have no symmetry under the interchange of pairs of electron coordinates belonging to different atoms. Thus, we cannot represent $\Psi^{(0)}$ by an expansion in the Φ_k because that expansion would be antisymmetric under the interchange of every pair of electron coordinates. Similarly, $\Psi(\lambda)$ cannot be totally antisymmetric for $\lambda \neq 1$ and, therefore, must have the form

$$\Psi(\lambda) = \sum_k C_k(\lambda)\Phi_k + \sum_l D_l(\lambda)u_l \quad (5)$$

when expanded in the eigenfunctions of \hat{H} . For $\lambda = 1$ all the D_l and all but one of the C_k must vanish if the series is to converge to a physical solution of \hat{H} . How difficult this may be to achieve can be seen by deriving parts of the physical and unphysical spectra of \hat{H}^0 and \hat{H} for some small molecules at $R = \infty$.

We consider H_2 and LiH. We have chosen the former because it is the example most commonly considered and because we want to emphasize that its spectrum is unrealistically simple. We have chosen LiH because it exhibits the overlapping physical and unphysical states which are typical of molecules having core electrons. For both molecules we exploit the available symmetries to resolve energy degeneracies as much as possible.

Spectra for H_2

We begin by constructing for H_2 the $^1\Sigma^+$ eigenfunctions of \hat{H}^0 which correspond to the levels shown in Figure 1. We assign electron 1 to nucleus a, electron 2 to nucleus b. One can easily verify that \hat{H}^0 does not commute with \hat{p}_{12} , the operator which interchanges the electron position coordinates 1 and 2, or with \hat{i} , the operator which inverts the electron coordinates in the midpoint of the molecular axis. Thus, the lowest energy eigenvalue of \hat{H}^0 is -1 hartree and the corresponding eigenfunction is $a_{1s}(1)b_{1s}(2)$, where a_{1s} is the hydrogen $1s$ function centered on A. We multiply this function by the singlet spin function.

The next eigenvalue of \hat{H}^0 is at $-5/8$ hartree. There are four Σ^+ functions. The degeneracy is reduced to two by invoking a special symmetry which \hat{H}^0 has for homonuclear diatomics. The special symmetry for H_2 is that \hat{p}_{12} commutes with

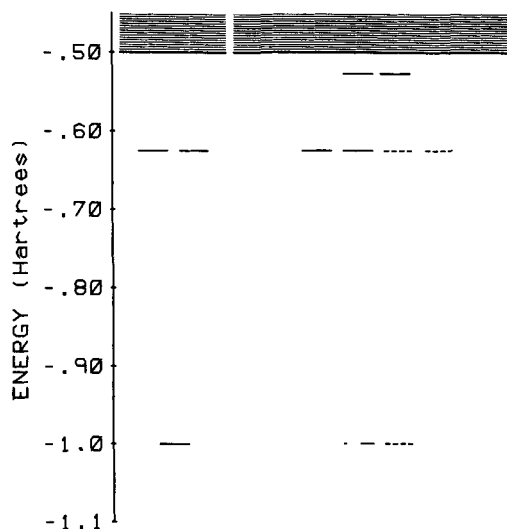


Figure 1. Energy level diagram showing selected eigenvalues of \hat{H}^0 and $\hat{H}^0 + \hat{V}$ for $^1\Sigma^+$ States of H_2 at $R = \infty$. The two lowest energy levels of \hat{H}^0 and the beginning of its continuum are represented on the left. The energy levels of $\hat{H}^0 + \hat{V}$ which correlate with these \hat{H}^0 states, and are degenerate with them, are represented on the right. In addition, there is a level just below the continuum which correlates with no eigenstate of \hat{H}^0 . Solid lines represent physical states, dashed lines, unphysical. The closely spaced lines represent the continuum.

\hat{H}^0 . The eigenvalues of \hat{p}_{12} are +1 and -1. The function $a_{1s}(1)b_{1s}(2)$ has the eigenvalue +1, so that we choose the corresponding first excited state functions and multiply them by the singlet spin function. The first excited level is doubly degenerate.

The eigenstates of \hat{H} are also represented in Figure 1. The construction of the physical states from the hydrogen atom states should be familiar, but some discussion is necessary because we must include the unphysical states and consider which eigenstates of \hat{H} can arise from the eigenstates of \hat{H}^0 singled out above. We restrict our attention to Σ_g^+ and Σ_u^+ functions of the position coordinates. The functions of each type are further classified as symmetric or antisymmetric under the interchange of the electron position coordinates. We multiply each function of the position coordinates by a spin eigenfunction, and classify them as physical if they satisfy the Pauli principle. Thus, in Figure 1 we show the lowest energy $^1\Sigma_g^+$ physical state and the lowest energy $^1\Sigma_u^+$ unphysical state. The latter function is a product of $a_{1s}(1)b_{1s}(2) - b_{1s}(1)a_{1s}(2)$ with the singlet spin function. Note that $a_{1s}(1)b_{1s}(2) - b_{1s}(1)a_{1s}(2)$ is an eigenfunction of \hat{p}_{12} and its eigenvalue is +1. There are four degenerate, first excited singlet states having the eigenvalue +1 for \hat{p}_{12} , two physical and two not. The physical continuum begins at $-1/2$ hartree.

There is one more physical $^1\Sigma^+$ state which we have to mention because there is no corresponding eigenstate of \hat{H}^0 . It arises from putting both electrons on one atomic center, i.e., by electron transfer. Thus, there must be an eigenstate of \hat{H} corresponding to the ground state of H^- . The state is doubly degenerate because there are two atomic centers. These physical $^1\Sigma^+$ states appear just below the continuum in Figure 1. If we had been considering $^3\Sigma^+$ states instead of singlets, however, we would have had to include unphysical states corresponding to the H^- spatial function multiplied by triplet spin functions.

Compare the spectra of \hat{H}^0 and \hat{H} for H_2 in Figure 1. Note that the nondegenerate ground state of \hat{H}^0 correlates with one physical and one unphysical state of \hat{H} . The doubly degenerate first excited state of \hat{H}^0 correlates with four \hat{H} states, two physical and two not. Figure 1 shows that the interaction between two H atoms does not result in a one-to-one mapping of atomic states onto molecular states, and in that sense it is not a problem well suited to solution by elementary perturbation methods. If all one knew about this problem were the energy levels shown in Figure 1, one would say that the perturbation \hat{V} is strong, not weak.

Spectra for LiH

In the analysis for LiH we arbitrarily assign electrons 1, 2, and 3 to Li and 4 to H. The Hamiltonian for the Li atoms, $\hat{h}_A = \hat{h}_{Li}$, operates on electron coordinates 1, 2, and 3. It includes all interactions between these electrons. Similarly, $\hat{h}_B = \hat{h}_H$ and operates only on electron coordinate 4. Electrons 1, 2, and 3 are indistinguishable because they both belong to Li. Electron 4 is distinguishable from the first three because it belongs to H. Thus, the product of a physical (fully antisymmetric) Li eigenfunction and a H-atom eigenfunction is an eigenfunction of \hat{H}^0 with all of the symmetry appropriate for that Hamiltonian. We use spin eigen-

functions of Li for electrons 1, 2, and 3, and a hydrogen atomic eigenfunction multiplied by a spin eigenfunction for electron 4. We spin couple the product functions to get spin eigenfunctions. In Figure 1 we have represented the two lowest energy $^1\Sigma^+$ levels of \hat{H}^0 and the beginning of the continuum. The lowest energy level is at -7.978 hartree, the sum of the Li and H ground-state energies. It is nondegenerate. The first excited $^1\Sigma^+$ energy level of \hat{H}^0 is at -7.910 hartree, which is the sum of the Li 2^2P energy and the H ground-state energy. This level is nondegenerate. The continuum begins at -7.780 hartree, which corresponds to ionizing Li. Note that the discrete states corresponding to ground state Li plus an H excited state lie in the continuum.

The task of constructing the eigenstates of \hat{H} is somewhat more difficult than for \hat{H}^0 . The easy states to locate are those which correlate with the states of \hat{H}^0 , including the continuum. For example, consider the lowest $^1\Sigma^+$ eigenfunction of \hat{H}^0 , which is a spin-coupled product of the Li 2^2S for electrons 1-3 with the H $1s$ function for electron 4. From this one function we can construct three more product functions by interchanging coordinate 4 with one of the three coordinates assigned to Li. From these four linearly independent functions we can form one totally antisymmetric function and three which belong to unphysical irreducible representations of the symmetric group. All four functions have the same energy as the lowest energy eigenfunction of \hat{H}^0 at infinite nuclear separation. We can construct in the same manner physical and unphysical eigenfunctions which correlate with the other discrete eigenstates of \hat{H}^0 .

Many other $^1\Sigma^+$ eigenstates of \hat{H} arise from the exchange of pairs of electrons between the two atoms, but they correlate with no eigenstates of \hat{H}^0 because they arise from an unphysical state of Li. Recall that the H electron is distinguishable from the Li electrons in the polarization approximation. The lowest energy unphysical state of Li is totally symmetric and can be thought of as a $1s^3$ state. We use the notation, however, $1s^2[1s]$ to remind us that one of the $1s$ electrons is different. We have found an upper bound of -8.591 hartree for the energy of this state by using as a trial function the symmetric projection of $\exp[-(\zeta_1 r_1 + \zeta_2 r_2 + \zeta_3 r_3)]$ and minimizing the energy with respect to the ζ 's. Thus, the lowest energy unphysical eigenstate of \hat{H} corresponds to a Li $1s^2[1s]$ plus an H $1s$. The energy of this state is less than -9.091 hartree. The state is nondegenerate because we require that the wave function be antisymmetric in the electron coordinates 1, 2, and 3 and that the state be a singlet. The first excited state corresponds to the Li $1s^2[1s]$ plus a H $2s$ or $2p$. This level is doubly degenerate. An infinite number of discrete states can be constructed in this manner by combining the Li $1s^2[1s]$ state with the discrete excited states of H. All of these states have lower energy than the physical ground state. Furthermore, a continuum of unphysical states of \hat{H} can be constructed by combining the Li $1s^2[1s]$ state with the continuum states of H. This unphysical continuum begins below -8.591 hartree, which is below the energy of the lowest physical state. Thus, the physical states we want to study by perturbation methods are higher in energy than an infinite number of unphysical, discrete states and are buried in a continuum of unphysical states.

In addition to the states described above, there are discrete, physical eigenstates of \hat{H} which correspond to no eigenstates of \hat{H}^0 . They are constructed by transferring an electron from one atom to the other, making a positive and a negative ion. There is the discrete physical $^1\Sigma^+$ state just below the physical continuum which corresponds to the $\text{Li}^+ 1s^2$ state combined with the $\text{H} 1s^2$ state. It has an energy of -7.807 hartree and is included in Figure 2. There is, also, a state which arises from the transfer of the H electron to the Li atom to form the physical Li^- ground state function, but it lies in the physical continuum since the ionization potential of H exceeds the electron affinity of Li (0.023 hartree). In addition to this physical Li^- state, unphysical states with the configurations $1s^2[1s]2s$, $1s^2[1s]2p$, etc., may exist, although we have no evidence that they do.

Figure 2 summarizes our results for the lowest, discrete, $^1\Sigma^+$ eigenstates of \hat{H}^0 and \hat{H} for LiH in the limit $R = \infty$. In addition, we have indicated where the physical and unphysical continua begin. We do not believe the spectra will be simpler at finite R . Note that where \hat{H}^0 gives one discrete state, \hat{V} creates four. In addition, \hat{V} creates an infinite number of discrete, unphysical states lying below the lowest physical state, plus an unphysical continuum which blankets the physical states. The interaction between Li and H must be very strong.

To understand how \hat{V} can be so strong yet look so weak, it is helpful to consider the LiH problem in more physical terms. We have to assume that the H atom's electron is distinguishable from those of the Li atom to be consistent with the polarization approximation. This means that the H electron does not have to obey

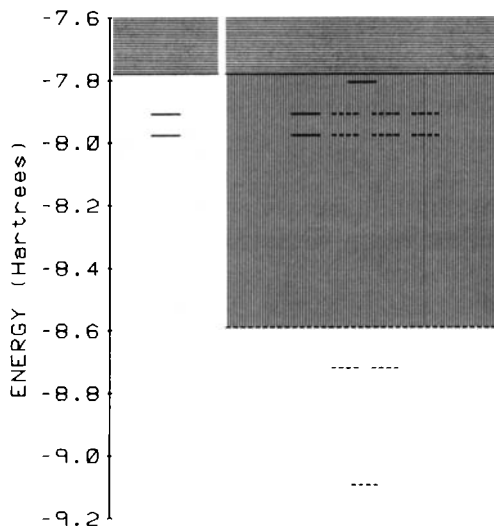


Figure 2. Energy level diagram showing selected eigenvalues of \hat{H}^0 and $\hat{H}^0 + \hat{V}$ for $^1\Sigma^+$ States of LiH at $R = \infty$. The closely spaced vertical lines represent the unphysical continuum. The other conventions are explained in the caption to Figure 1. The two lowest energy, unphysical levels of $\hat{H}^0 + \hat{V}$ are also represented on the right. The single physical state just below the continuum correlates with no state of \hat{H}^0 .

the Pauli principle, it can fall into the Li core. The Pauli principle forbids it to do so in the real world, so that we cannot see the actual strength of the interaction.

It should be clear without discussion of other examples that whenever one of the interacting atoms has a core, there will be discrete unphysical states lower in energy than the physical ground state of the system, and the physical states will lie in a continuum of unphysical states [9]. The H_2 problem, as can be seen by comparing Figures 1 and 2, is atypical and, therefore, a poor test problem for perturbation methods.

We find it difficult to look at Figure 2 and believe that one can determine any of the physical eigenenergies and eigenfunctions of \hat{H} by perturbation methods starting from the eigenstates of \hat{H}^0 . The situation would be different if the unphysical states could not mix with the physical ones. This would happen if one chose the unperturbed problem so that electron indistinguishability were maintained for all values of the coupling parameter λ . The problem is to do this and to keep the separated atoms as the unperturbed problem. Jansen [16] and others [17] have tried to do it by transforming \hat{H}^0 , but there is no agreement on the precise form of the transforming operator.

Eisenschitz–London Class Theories

We distinguish two major classes of EPT based on the concept of a *primitive wave function*, i.e., a function which is not an eigenfunction of \hat{H} , but which, when symmetry projected, becomes an eigenfunction [18]. When only one symmetry projection of the primitive wave function is an eigenfunction of \hat{H} , we say that it belongs to the Eisenschitz–London (EL) class [11,19]. If each symmetry projection produces an \hat{H} eigenfunction, we say that it belongs to the Hirschfelder–Silbey (HS) class [20,21]. In this section we analyze only those theories which determine an EL class primitive function as the eigenfunction of an *effective* Hamiltonian.

The goal of our analysis is to determine the extent to which the various exchange perturbation theories transform the intermolecular perturbation problem into one in which there is a one-to-one mapping of the discrete unperturbed states onto the perturbed states, and vice versa. In effect, we have to solve the perturbation problem to infinite order in the limit that the expansion parameter $\lambda = 1$. This has meant that we could only consider theories which define the primitive function as the eigenfunction of an effective Hamiltonian. Theories which are not based explicitly on the solution of an eigenvalue problem, or which have only been defined by a perturbation expansion, have not been studied. The original EL theory [11], which explicitly determines the wave function only through first order, is one we could not study.

Hirschfelder's Equation

Hirschfelder [22] based his version of the EL and Van der Avoird [23] theories on his Eq. (3), i.e., on finding the eigenfunctions and eigenvalues of the operator, in our notation, $\hat{H}^0 + \hat{\mathcal{A}}\hat{V} - (E_1 - E_1^{(0)})\hat{\mathcal{A}}$. We focus here on the operator

$$\hat{\mathcal{H}}_H = \hat{H}^0 + \hat{\mathcal{A}}\hat{V} \quad (6)$$

since the other term acts merely as a level shift operator, the effect of which can be taken into consideration later. One can easily show that if F is an eigenfunction of $\hat{\mathcal{H}}_H$, then $\hat{\mathcal{A}}F$ is an eigenfunction of \hat{H} .

The spectrum of $\hat{\mathcal{H}}_H$ is easily determined by evaluating its matrix elements with the physical and unphysical eigenfunctions of \hat{H} defined in the previous section. We find that $\langle \Phi_k | \hat{\mathcal{H}}_H | \Phi_l \rangle = E_k \delta_{k,l}$, $\langle \Phi_k | \hat{\mathcal{H}}_H | u_l \rangle = 0$, $\langle u_k | \hat{\mathcal{H}}_H | \Phi_l \rangle = \langle u_l | \hat{H}^0 | \Phi_l \rangle$, and $\langle u_k | \hat{\mathcal{H}}_H | u_l \rangle = \langle u_k | \hat{H}^0 | u_l \rangle$. It is useful to transform the unphysical functions so that the matrix of $\langle u_k | \hat{H}^0 | u_l \rangle$ elements is diagonalized. Let the resultant eigenfunctions and eigenvalues be respectively U_k and ω_k . The matrix of $\hat{\mathcal{H}}_H$ in the Φ_k , U_k -basis is zero above the diagonal, and, therefore, the eigenvalues of $\hat{\mathcal{H}}_H$ are the physical eigenvalues of \hat{H} plus the ω_k . Note that eigenfunctions belonging to the ω_k , provided that they are not degenerate with physical eigenstates, can have no antisymmetric projection.

The spectrum of $\hat{\mathcal{H}}_H$ is considerably simpler than that found in the polarization approximation. By the separation theorem [24], the eigenvalues ω_k , ordered so that $\omega_k \leq \omega_{k+1}$, must be upper bounds to the similarly ordered eigenvalues of \hat{H}^0 . At infinite R , this means that $\hat{\mathcal{H}}_H$ has, at worst, two eigenvalues, $E_k = E_k^{(0)}$ and $\omega_k = E_k^{(0)}$, where \hat{H}^0 has one. The discrete unphysical states below the lowest physical states, and the continuum of unphysical states in which the physical states are buried in the polarization approximation, are not in the lower spectrum of $\hat{\mathcal{H}}_H$. To this extent $\hat{\mathcal{H}}_H$ is a better starting point for a perturbation theory of intermolecular interactions than is $\hat{H}^0 + \hat{V}$; its spectrum correlates better with that of \hat{H}^0 .

One can say more about the relationship between the ω_k and the $E_k^{(0)}$ at infinite R . Note that the ω_k are the eigenvalues of $(1 - \hat{\mathcal{A}})\hat{H}^0(1 - \hat{\mathcal{A}})$ since $1 - \hat{\mathcal{A}} = \sum_k |u_k\rangle\langle u_k|$. Thus, by the variational theorem, $\omega_1 \leq \langle \Psi_1^{(0)} | (1 - \hat{\mathcal{A}})\hat{H}^0(1 - \hat{\mathcal{A}}) | \Psi_1^{(0)} \rangle$. Note, also that $1 - \hat{\mathcal{A}} = 1 - \sum_k |\Omega_k\rangle\langle \Phi_k|$. Let $\mathcal{S} = 1 - |\Phi_1\rangle\langle \Phi_1|$. By the separation theorem [24], the eigenvalues of $\mathcal{S}\hat{H}^0\mathcal{S}$, ordered from smallest to largest, must be lower bounds to the ω_k and upper bounds to the $E_k^{(0)}$. Furthermore, since $\Phi_k = \hat{\mathcal{A}}\Psi_k^{(0)} / \langle \Psi_k^{(0)} | \hat{\mathcal{A}} | \Psi_k^{(0)} \rangle^{1/2}$ at infinite R , the $\Psi_k^{(0)}$ diagonalize $\mathcal{S}\hat{H}^0\mathcal{S}$. The eigenvalues of $\mathcal{S}\hat{H}^0\mathcal{S}$ are $\langle \Psi_1^{(0)} | \mathcal{S}\hat{H}^0\mathcal{S} | \Psi_1^{(0)} \rangle$ and $E_2^{(0)}$, $E_3^{(0)}$, One may verify that the first of these is identical to the upper bound to ω_1 given above. In the Appendix we show that, for LiH, $\langle \Psi_1^{(0)} | \mathcal{S}\hat{H}^0\mathcal{S} | \Psi_1^{(0)} \rangle$ lies in the physical continuum. Thus, the lowest eigenvalue of $\mathcal{S}\hat{H}^0\mathcal{S}$ for LiH must be greater than or equal to $E_2^{(0)}$, and there is, consequently, a one-to-one correspondence between the lowest eigenvalue of $\hat{\mathcal{H}}_H$ and the lowest eigenvalue of \hat{H}^0 . Unfortunately, this correspondence is achieved only because LiH has so few electrons.

The dependence of $\langle \Psi_1^{(0)} | \mathcal{S}\hat{H}^0\mathcal{S} | \Psi_1^{(0)} \rangle$ on the number of electrons follows from the definition $\hat{\mathcal{A}} = a(N_A, N_B) \sum_{\hat{p}} (-1)^{|\hat{p}|} \hat{p}$, where $a(N_A, N_B) = N_A! |N_B| / N!$ and the sum is over all interatomic interchanges of position-spin coordinates. When $R = \infty$, the functions $\hat{p}\Psi_k^{(0)}$ and $\hat{p}'\Psi_k^{(0)}$ do not overlap if $\hat{p} \neq \hat{p}'$, which means that $\langle \Psi_1^{(0)} | \hat{p}\hat{H}^0\hat{p}' | \Psi_1^{(0)} \rangle$ vanishes. Therefore,

$$\begin{aligned} \langle \Psi_1^{(0)} | \mathcal{S} \hat{H}^0 \mathcal{S} | \Psi_1^{(0)} \rangle &= E_1^{(0)} (1 - 2a(N_A, N_B)) \\ &+ a(N_A, N_B)^2 \sum_{\hat{p}} \langle \Psi_1^{(0)} | \hat{p} \hat{H}^0 \hat{p} | \Psi_1^{(0)} \rangle \end{aligned} \quad (7)$$

The coefficient $a(N_A, N_B)$ is only 1/4 for LiH, but 1/184,756 for Ne₂. Thus, as the total number of electrons in the system increases, we can expect the matrix element in Eq. (7) to approach $E_1^{(0)}$ from above. This means that ω_1 approaches $E_1^{(0)}$ and that \mathcal{H}_H is going to have a pair of almost degenerate eigenvalues where \hat{H}^0 has one. We conclude that \hat{H}_H as a starting point for the development of a perturbation theory of intermolecular interactions is a major step in the right direction, but it is not a complete solution to the problems seen in the polarization approximation.

Up to this point we have ignored the effect of that the level shift operator $-(E_1 - E_1^{(0)})\hat{\mathcal{A}}$ has on the spectrum of \mathcal{H}_H . Basically, it shifts all of the physical eigenvalues of \mathcal{H}_H higher if the interaction energy is negative, lower if positive. Thus, if the ground state potential curve is attractive, the physical eigenvalues are shifted in the direction of the ω_k , thus increasing the likelihood that there will be two eigenvalues of \mathcal{H}_H , whereas \hat{H}^0 has only one. The level shift operator was introduced by Hirschfelder to make the first-order energy equal to the Heitler-London result.

Peierls [25] developed an effective Hamiltonian for symmetry adapted perturbation theories which is related to \mathcal{H}_H . Peierls Hamiltonian is $\mathcal{H}_P = \hat{H}^0 + \hat{\mathcal{P}}\hat{V}$, where $\hat{\mathcal{P}}$ is the *standardization operator*. The one property of $\hat{\mathcal{P}}$ that is important to us is that $\hat{\mathcal{A}}\hat{\mathcal{P}} = \hat{\mathcal{A}}$. Operators having this property are easily constructed from permutation operators [26]. When one calculates the matrix elements of \mathcal{H}_P with the Φ_k, u_k functions, one finds that they have exactly the same values as those of \mathcal{H}_H given above. Thus, even though $\hat{\mathcal{P}} \neq \hat{\mathcal{A}}$, the Hirschfelder and Peierls Hamiltonians must have the same eigenfunctions.

The Hirschfelder and Peierls effective Hamiltonians are special cases of the general Hamiltonian defined in Klein's Eq. (C.1) [7], $\mathcal{H}_G = \hat{H}^0 + \hat{V} + (1 - \hat{\mathcal{A}})\hat{f}$, where \hat{f} is an arbitrary operator. The effect of this operator can be determined by calculating the matrix elements of \mathcal{H}_G with the Φ_k and u_k . The ω_k are then determined by diagonalizing the matrix of $\langle u_k | \hat{H}^0 + \hat{V} + \hat{f} | u_l \rangle$. Clearly, a suitable choice of \hat{f} can give ω_k 's which are higher in energy than the discrete, bound states of \hat{H} . The problem is to choose \hat{f} so that the eigenfunctions of discrete states are related to the $\Omega_k^{(0)}$, so that the first order energy is the Heitler-London energy, etc.

Localized Wave Function Hamiltonian

An EL class perturbation theory has been developed on the basis of the localized wave function (LW) effective Hamiltonian [19]. The LW equation is not a special case of the general EL effective Hamiltonian \mathcal{H}_G defined above. Basically, an EL LW primitive function F is defined to be *least distorted* from a $\Psi_k^{(0)}$ in the sense that it minimize $\langle F | \hat{H}^0 | F \rangle / \langle F | F \rangle$ under the constraint that $\hat{\mathcal{A}}F$ is proportional to one and only one Φ_k . In contrast, there is no requirement in the theories con-

sidered in the previous subsection that there be any optimum relationship between the primitive function and $\Psi_1^{(0)}$. The EL LW-based perturbation theory gives the same wave function through first order, and the same energy through second order, as the original EL theory and that based on $\hat{\mathcal{H}}_H$. In higher orders, differences appear.

The effective Hamiltonian for EL LWS is

$$\hat{\mathcal{H}}_L = \hat{H}^0 + \hat{V} - \hat{Q}_L \hat{V} \hat{Q}_L \quad \text{with} \quad \hat{Q}_L = 1 - \hat{\mathcal{A}} + \hat{\mathcal{A}}|F\rangle \frac{1}{\langle F|F\rangle} \langle F|\hat{\mathcal{A}} \quad (8)$$

Note that \hat{Q}_L is a projection operator. One can prove that if F is an eigenfunction of $\hat{\mathcal{H}}_L$, then $\hat{\mathcal{A}}F$ is an eigenfunction of \hat{H} and is least distorted from an eigenfunction of \hat{H}^0 in the sense defined above. Only one projection of F is an eigenfunction of \hat{H} . In what follows, we assume that $\hat{\mathcal{A}}F \propto \Phi_1$ unless otherwise stated.

The spectrum of $\hat{\mathcal{H}}_L$ can be deduced with the aid of \hat{Q}_L and $\hat{P}_L = 1 - \hat{Q}_L$. Note that from (8) it follows that $\hat{Q}_L = |\Phi_1\rangle\langle\Phi_1| + \sum_k |u_k\rangle\langle u_k|$, and that $\hat{P}_L = \sum_{k \neq 1} |\Phi_k\rangle\langle\Phi_k|$. It follows from (8) that $\hat{Q}_L \hat{\mathcal{H}}_L \hat{Q}_L = \hat{Q}_L \hat{H}^0 \hat{Q}_L$, $\hat{P}_L \hat{\mathcal{H}}_L \hat{P}_L = \hat{P}_L \hat{H} \hat{P}_L$, and $\hat{P}_L \hat{\mathcal{H}}_L \hat{Q}_L = 0$. Thus, the discrete spectrum of $\hat{\mathcal{H}}_L$ includes the discrete eigenvalues of $\hat{P}_L \hat{H} \hat{P}_L$, i.e., all of the physical eigenvalues of \hat{H} except E_1 . The rest of the discrete spectrum of $\hat{\mathcal{H}}_L$ is determined by the eigenvalues of $\hat{Q}_L \hat{H}^0 \hat{Q}_L$, which, by the separation theorem [24], must be upper bounds to the eigenvalues of \hat{H}^0 . Thus, at large R , the lowest eigenstate of \hat{H}^0 correlates with the lowest of $\hat{\mathcal{H}}_L$. The higher energy eigenstates of \hat{H}^0 may correlate, however, with two eigenstates of $\hat{\mathcal{H}}_L$ for the same reasons that each eigenstate of \hat{H}^0 could correlate, in general, with two eigenstates of $\hat{\mathcal{H}}_H$. Thus, the $\hat{\mathcal{H}}_L$ discrete spectrum correlates better with the \hat{H}^0 spectrum than does the $\hat{\mathcal{H}}_H$ spectrum by one state, the lowest.

The only other EL class EPT which defines its primitive function so that it has an optimized relationship to $\Psi_1^{(0)}$ is due to Chipman [27]. He defines his primitive function to have maximum overlap with $\Psi_1^{(0)}$. Unfortunately, his primitive function is not the eigenfunction of an effective Hamiltonian, so that we cannot determine its spectrum.

We conclude that EL class EPTs can completely eliminate the problems noted by Clavierie and by Morgan and Simon: the Hirschfelder, Peierls, and LW effective Hamiltonians have no unphysical eigenstates lower in energy than the lowest states of \hat{H}^0 and no continuum of unphysical states overlaying the lowest physical states. It is not obvious that all EL class theories achieve this improvement relative to the polarization approximation. None of the effective Hamiltonians examined, however, gives a one-to-one mapping of its discrete states onto those of \hat{H}^0 for larger systems. For the specific example of LiH, because it has so few electrons, at least the two lowest discrete states of $\hat{\mathcal{H}}_H$, $\hat{\mathcal{H}}_P$, and $\hat{\mathcal{H}}_L$ map onto the two lowest of \hat{H}^0 at infinite separation. Only for the LW effective Hamiltonian, however, is it clear for larger systems that there is just one eigenstate in correspondence with the lowest of \hat{H}^0 .

Hirschfelder-Silbey Class Theories

In the HS class of exchange perturbation theories each symmetry projection of the primitive wave function is required to be an eigenfunction of \hat{H} [20,21]. A

desirable consequence of this requirement is that an HS class perturbation theory must give correctly the asymptotic $1/R$ expansion. For this reason it has been argued that HS class theories are the only acceptable perturbation theories for intermolecular interactions [28,29]. On the other hand, Chipman [30] has argued that requiring the correct asymptotic behavior is as arbitrary as any other requirement that one might impose. We show below that two HS class effective Hamiltonians do almost nothing to improve on the polarization approximation. Neither has an effect on the discrete unphysical states below the physical states, nor on the unphysical continuum, which is probably why they give the correct asymptotic $1/R$ behavior.

Hirschfelder's Hamiltonian

The original HS perturbation theory was reformulated by Hirschfelder [22], [see his Eq. (40)] as the problem of finding the eigenfunction F of an effective Hamiltonian. His Hamiltonian can be defined in terms of the operators \hat{e}_{ij}^{μ} , which form a matrix basis for the irreducible representations of the symmetric group [31]. For our purposes one needs to know only that the superscript μ labels the irreducible representations, that $\hat{\mathcal{A}}$ is one of the \hat{e}_{ij}^{μ} , and that $\hat{e}_{ij}^{\mu}\hat{e}_{kl}^{\nu} = \delta_{\mu\nu}\delta_{jk}\hat{e}_{il}^{\mu}$. Hirschfelder's Hamiltonian is

$$\hat{\mathcal{H}}_H = \hat{H} - \sum_{\mu,i} (E_{[1]}^{\mu} - E_1^{(0)}) \hat{e}_{ii}^{\mu} \quad (9)$$

where $E_1^{(0)}$ is the lowest energy, physical eigenvalue of \hat{H}^0 , the sum is over all irreducible representations of the symmetric group for the specific system, and over all rows of each irreducible representation. The symbol $E_{[1]}^{\mu}$ represents the energy eigenvalue of \hat{H} belonging to the μ th irreducible representation and correlating with $E_1^{(0)}$ at infinite separation. It is important to recognize that any eigenfunction of \hat{H} is also an eigenfunction of $\hat{\mathcal{H}}_H$. The effect of the operator sum in (9) is to shift all \hat{H} eigenvalues belonging to the same irreducible representation by the same amount. It also makes degenerate all eigenfunctions of \hat{H} which correlate with $\Psi_1^{(0)}$. This permits these functions to mix in forming F , but how they mix is determined by the perturbation equations. The Hirschfelder Hamiltonian has no effect on the unphysical discrete and continuum states, which means that they pose the same problem that they did in the polarization approximation. For this reason we believe that the original HS theory is no improvement on the polarization approximation.

Localized Wave Function Hamiltonian

An HS class LW has been defined [21,32] and a perturbation theory has been based on it. The HS LW primitive function F is defined to be *least distorted* from $\Psi_1^{(0)}$ by requiring that it minimize $\langle F|\hat{H}^0|F\rangle/\langle F|F\rangle$ and belong to the HS class of primitive functions. Let

$$\hat{Q}_L = \sum_{\mu,i} \hat{e}_{ii}^{\mu} |F\rangle \frac{1}{\langle F|\hat{e}_{ii}^{\mu}|F\rangle} \langle F|\hat{e}_{ii}^{\mu}$$

where the sum is over those values of μ and i for which $\langle F | \hat{e}_i^\mu | F \rangle \neq 0$. It has been shown that if F is an eigenfunction of

$$\hat{\mathcal{H}}_L = \hat{H}^0 + \hat{V} - \hat{Q}_L \hat{V} \hat{Q}_L \quad (10)$$

then $\hat{e}_i^\mu F$, if it does not vanish, is an eigenfunction of \hat{H} and F is least distorted from $\Psi_1^{(0)}$ in the above sense [32]. Thus, \hat{Q}_L is a sum over a subset of the \hat{H} eigenfunctions, a subset which we call here the HS set.

All eigenfunctions of \hat{H} except those belonging to the HS set are also eigenfunctions of $\hat{\mathcal{H}}_L$. The entire effect of the $\hat{Q}_L \hat{V} \hat{Q}_L$ term in (10) is to mix the functions in the HS set and change the energy eigenvalues. It leaves the discrete and continuum unphysical states where they were in the polarization approximation. The lowest energy HS primitive function is higher in energy than the lowest energy, unphysical states and is buried in the unphysical continuum. Thus, the HS LW theory is no improvement on the polarization approximation.

Although neither of the HS class effective Hamiltonians represents an improvement on the polarization approximation, this does not mean that no HS class theory can improve significantly on the polarization approximation. One can see that the only change required would be to add to $\hat{\mathcal{H}}_H$ or $\hat{\mathcal{H}}_L$ an operator which would raise the energies of all u_k except those in the HS set. Unfortunately, we have yet to find a suitable operator.

Discussion

We have focused in this paper on the spectra of N -electron effective Hamiltonians which can be used as starting points for the development of a perturbation theory. We have restricted our study to those Hamiltonians which exploit only the electronic exchange symmetry, a symmetry common, of course, to all electronic systems. Our narrow focus has been rewarded, however, by allowing us to see what has and has not been accomplished by some proposed EPTs. It remains to be seen if the failings of any of these theories can be corrected; knowing how they fail is a first step in that direction. In the following paragraphs we touch on aspects of the problem not discussed elsewhere in this paper.

We have not considered how site symmetry can be exploited because we wanted to see what could be accomplished using only the electronic exchange symmetry. We excluded it, also, because site symmetry and exchange symmetry can combine to give other symmetries, e.g., as in our discussion of the H_2 states in the second section. Site symmetry has been exploited by Mann and Privman [33] to develop a perturbation theory which, although apparently limited to one-electron problems, has a very desirable property. It has no bound state, spurious (= unphysical) solutions. Perhaps their approach could be incorporated into the N -electron problem and exploited along with exchange symmetry. It might be the way to get rid of the unphysical states still left in the EL EPTs.

We remarked in the previous subsection that the HS class of EPTs give the correct, asymptotic $1/R$ expansion of the interaction energy. The EL class theories give an incorrect asymptotic behavior *through second order*, which is the basis for the ar-

gument that they are inferior to the HS class [29]. However, it has been found in calculations on H_2 that when the third order energy is added, the error in the EL interaction energies at $R \geq 8$ bohr are reduced by 75% or more [34]. This suggests that the correct asymptotic behavior can be obtained by summing the energy to higher order. If this is the case, do we really have to require that the second-order energy give the correct asymptotic behavior?

A major assumption that we have made is that the less disparity there is between the spectra of the unperturbed and perturbed Hamiltonians, the better behaved the perturbation theory is likely to be. We have numerical evidence, unpublished calculations on HeH^+ , that suggest that this is a reasonable assumption, but it is an assumption that should be tested more generally. We have assumed, also, that if we can shift the energies of the unphysical solutions into the physical continuum, they cannot affect the physical solutions. This assumption should be tested, too. We have omitted from our analysis any consideration of the effect of finite R , which should certainly be investigated. We plan to study these questions using a model in which the Hamiltonians and other operators are transformed into matrices in a basis of N -electron functions, each of which is the product of two Slater determinants, one for each group. We have completed a prototype, bideterminantal, configuration interaction program which will permit us to study small diatomics using any of the perturbation theories considered in the third and fourth sections. The program cannot produce a continuum of unphysical states like that pictured in Figure 2, but with tens of thousands of configurations, most will be unphysical.

Although we have considered in this paper only the limit of infinite separation in diatomic systems, it has been possible to reach certain, specific conclusions. It is clear from comparing Figures 1 and 2 that calculations on systems made up only of H and He atoms are not realistic tests of perturbation methods. We have shown that certain EL class EPTs dramatically, but not totally, alleviate the problems with unphysical states encountered in the polarization approximation. The HS class EPTs, however, were ineffectual in this regard. In short, we have learned a bit more about the nature of the intermolecular perturbation problem.

Appendix

The definition of \mathcal{S} in the third section and Eq. (7) are the starting points for estimating lower bounds to the ω_k at $R = \infty$. Let $\chi_{k,l} = \Psi_k^{(0)}$ and $\chi_{k,n} = \hat{p}_n \Psi_k^{(0)}$, where \hat{p}_n interchanges electrons between A and B. There are $1/a(N_A, N_B)$ distinct interchange operators.

For LiH it helps to be more specific. Let $\phi_{k\alpha}$ be the k th Li state function with $M_S = +\frac{1}{2}$ and let b_β be the downspin, 1s function of H. We can write $\chi_{k,l}(1, 2, 3, 4) = (1/\sqrt{2})[\phi_{k\alpha}(1, 2, 3)b_\beta(4) - \phi_{k\beta}(1, 2, 3)b_\alpha(4)]$, $\chi_{k,2}(1, 2, 3, 4) = \chi_{k,l}(4, 2, 3, 1), \dots$, and $\chi_{k,4}(1, 2, 3, 4) = \chi_{k,l}(1, 2, 4, 3)$. Thus, the totally antisymmetric eigenfunctions of \hat{H} at $R = \infty$ are $\Phi_k = \frac{1}{2}[\chi_{k,l} - \chi_{k,2} - \chi_{k,3} - \chi_{k,4}]$. Using this notation, and noting that the value of the matrix element depends only on the relative spin orientations, Eq. (7) becomes for LiH $\langle \Psi_1^{(0)} | \mathcal{S} \hat{H}^0 \mathcal{S} | \Psi_1^{(0)} \rangle = \frac{9}{16} E_1^{(0)} + \frac{3}{16} \langle \chi_{1,2} | \hat{H}^0 | \chi_{1,2} \rangle$ since the matrix element of \hat{H}^0 with $\chi_{1,1}$ is $E_1^{(0)}$, and with each

of the other three $\chi_{1,n}$ it is $\langle \chi_{1,2} | \hat{H}^0 | \chi_{1,2} \rangle = \langle \phi_{1\alpha}(4, 2, 3) b_\beta(1) | \hat{H}^0 | \phi_{1\alpha}(4, 2, 3) b_\beta(1) \rangle$. In \hat{H}^0 electrons 1, 2, and 3 are on Li, and 4 is on H. Let \hat{t}_i be the kinetic energy operator for electron i . Since the atoms are infinitely far apart,

$$\langle \chi_{1,2} | \hat{H}^0 | \chi_{1,2} \rangle = \langle \phi_{1\alpha}(4, 2, 3) | \hat{h}_{\text{Li}^+}(2, 3) + \hat{t}_4 | \phi_{1\alpha}(4, 2, 3) \rangle + \langle b_\beta(1) | \hat{t}_1 | b_\beta(1) \rangle$$

By the virial theorem [35], $\langle \phi_{1\alpha}(4, 2, 3) | \hat{t}_4 | \phi_{1\alpha}(4, 2, 3) \rangle = -\frac{1}{3} E(\text{Li } 1s^2 2s)$. One can easily show that $\langle \phi_{1\alpha}(4, 2, 3) | \hat{h}_{\text{Li}^+}(2, 3) | \phi_{1\alpha}(4, 2, 3) \rangle \geq E(\text{Li } 1s^2)$. Thus, we conclude that $\langle \Psi_1^{(0)} | \hat{\mathcal{S}} \hat{H}^0 \hat{\mathcal{S}} | \Psi_1^{(0)} \rangle \geq -5.195$ hartrees, which is well up in the physical continuum. This means, referring back to the argument in the fourth section, that $\omega_1 \geq E_2^{(0)}$.

The above argument can be extended for LiH to show that $\omega_1 \geq E_3^{(0)}$ by setting $\hat{\mathcal{S}} = 1 - |\Phi_1\rangle\langle\Phi_1| - |\Phi_2\rangle\langle\Phi_2|$. Since $R = \infty$ and the first excited state of Li has P symmetry, $\langle \Phi_1 | \hat{H}^0 | \Phi_2 \rangle = 0$, and we find that both $\langle \Psi_1^{(0)} | \hat{\mathcal{S}} \hat{H}^0 \hat{\mathcal{S}} | \Psi_1^{(0)} \rangle$ and $\langle \Psi_2^{(0)} | \hat{\mathcal{S}} \hat{H}^0 \hat{\mathcal{S}} | \Psi_2^{(0)} \rangle$ are in the physical continuum.

A similar argument works for obtaining lower bounds on the eigenvalues of $\hat{Q}_L \hat{H}^0 Q_L$. One simply replaces Q_L with $1 - |\Phi_2\rangle\langle\Phi_2| - |\Phi_3\rangle\langle\Phi_3|$ and calculates the matrix elements of $\hat{Q}_L \hat{H}^0 Q_L$ with the $\Psi_k^{(0)}$.

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