Journal of Mathematical Chemistry 10(1992)1-23

THE PROBLEM OF UNPHYSICAL STATES IN THE THEORY OF INTERMOLECULAR INTERACTIONS

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Abstract

It was shown by Claverie that the interactions between atoms and molecules make unphysical electronic solutions of the Schrödinger equation accessible in perturbation calculations of intermolecular interactions, accessible in the sense that the perturbation expansion is likely to converge to an unphysical solution if it converges at all. This is a difficult problem because there are generally an infinite number of unphysical states with energies below that of the physical ground state. We have carried out configuration interaction calculations on LiH of both physical and unphysical states. They show that avoided crossings occur between physical and unphysical energy levels as the interaction between the two atoms is turned on, i.e. as the expansion parameter λ is increased from 0 to 1. The avoided crossing for the lowest energy state occurs for $\lambda < 0.8$, implying that the perturbation expansion will diverge for larger values of λ. The behavior of the energy levels as functions of λ is shown to be understandable in terms of a two-state model. In the remainder of the paper, we concentrate on designing effective Hamiltonians which have physical solutions identical to those of the Schrödinger equation, but which have no unphysical states of lower energy than the physical ground state. We find that we must incorporate ideas from the Hirschfelder-Silbey perturbation theory, as modified by Polymeropoulos and Adams, to arrive finally at an effective Hamiltonian which promises to have the desired properties, namely, that all unphysical states be higher in energy than the physical bound states, that the first and higher order corrections to the energy vanish in the limit $R = \infty$, that the leading terms of the asymptotic $1/R$ expansion of the energy be given correctly in second order, and that the overlap between the zeroth order wave function and the corresponding eigenfunction of the effective Hamiltonian be close to one.

1. Introduction

On the basis of physical evidence, the interactions between atoms and molecules have generally been regarded as weak and, thus, particularly well suited for study by perturbation methods. It is clear from the work of Claverie [1], and Morgan and Simon [2], however, that in terms of the mathematical theory, the interactions must be very strong, because they create an infinite number of unphysical states of lower energy than the physical ground state of most assemblies of atoms and molecules. These lower energy states are unphysical in the sense that the antisymmetric projections of their wave functions are identically zero. They have played no important role in

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the theory of electronic structure because they are inaccessible from the physical states, the interactions between electrons being symmetric in the electronic coordinates. However, in a theory in which one distinguishes between groups of electrons to the extent that the electron–electron interactions depend on the group to which each electron is assigned, the physical and unphysical states may mix so that one ultimately obtains an unphysical solution [1]. This is a fundamental barrier which any theory of intermolecular interactions should attempt to overcome. We report here what we have learned so far in trying to overcome it.

In a recent paper [3], we derived explicitly for the Hamiltonian of the LiH molecule at infinite internuclear separation both the unphysical and physical spectrum. We showed that there were an infinite number of bound, unphysical states lower in energy than the physical ground state, and a continuum of unbound, unphysical states beginning below the energy of the physical ground state. This is exactly what Morgan and Simon, without explanation, said was true for any system containing at least one atom with an atomic number greater than two [2]. In the light of this, it is difficult to imagine that any perturbation theory of intermolecular interactions can be correct if it is based on dividing the electronic Hamiltonian of a complex system into an unperturbed Hamiltonian $\hat{H}^0$ and a perturbation $\hat{V}$, with $\hat{H}^0$ defined to be the sum of the Hamiltonians for groups of electrons, specific electrons being assigned to each group. This is exactly what is done in the *polarization approximation*, the solution being determined by a Rayleigh–Schrödinger expansion. Claverie [1] made it quite clear that the polarization approximation makes the unphysical states accessible, so that if the expansion converges, it must be to the lowest energy unphysical state when the unperturbed function is the lowest energy eigenfunction of $\hat{H}^0$. He did not examine, however, alternative perturbation methods.

In the same paper, we examined several of the exchange perturbation theories that have been proposed over the last twenty-five years. The method we used allowed us to consider only those theories which were based on effective Hamiltonians. We derived the spectra of these effective Hamiltonians for LiH at infinite nuclear separation to see if they resolved the unphysical-states problem that invalidates the polarization approximation. The Hirschfelder–Silbey method [4,5], as modified by Polymeropoulos and Adams [6], is based on an effective Hamiltonian which has a spectrum differing insignificantly from the Schrödinger Hamiltonian and, thus, is not an improvement on the polarization approximation. The Eisenschitz–London type theories of Hirschfelder [5], Peierls [7], and Polymeropoulos and Adams [8], on the other hand, all shift the unphysical states up in energy so that there is a one-to-one correspondence between the lowest energy eigenstate of $\hat{H}^0$ and the lowest energy eigenstate of each effective Hamiltonian. In fact, the last named gave also a one-to-one correspondence between the first excited states. We showed, however, that in diatomic systems, as the number of electrons increase, the unphysical states move down in energy, approaching from above the lowest physical energy for the Hirschfelder and Peierls Hamiltonians, the next to lowest for the Polymeropoulos–Adams Hamiltonian. Thus, the best that has come out of the work on exchange perturbation theory to date are theories which may work for the physical ground state. We do not feel that this is a satisfactory achievement, although it is remarkable that any of the proposed methods even partially solved the unphysical-states problem since there appears to have been no conscious effort to do so.

In the next section we present the results of calculations of the eigenvalues of $\hat{H}^0 + \lambda \hat{V}$ for LiH as functions of λ using an unconventional configuration interaction method, one which yields unphysical as well as physical solutions for $\lambda = 1$. The calculations clearly show what happens to the eigenvalues of $\hat{H}^0 + \lambda \hat{V}$ as the coupling parameter λ is increased from zero to one. In particular, the lowest energy eigenstate of $\hat{H}^0$ is transformed continuously into the lowest unphysical eigenstate of $\hat{H}^0 + \hat{V}$, just as Claverie [1] argued it would be. The graph of the $E_k(\lambda)$ versus λ shows many avoided crossings, and an interesting "persistence" of eigenvalues through avoided crossings. By persistence, we mean that $E_1(\lambda)$, for example, is almost a straight line before the first avoided crossing, and that after that avoided crossing, $E_2(\lambda)$ approximately continues that straight line. A similar observation applies to the second avoided crossing,t'that between E_2 and E_3, and to many other avoided crossings as well. This behavior becomes more pronounced as the nuclear separation R increases.

In section 3, we explain why one should expect the eigenvalues to persist after avoided crossings. Our explanation suggests, also, why the polarization approximation gives the correct asymptotic $1/R$ expansion [2,9]. On the other hand, our analysis gives no assurance that the second-order polarization approximation energy is meaningful at finite R. It is apparent that the expansion of $E_k(\lambda)$ in a Taylor series about $\lambda = 0$ cannot converge beyond the point at which the first avoided crossing occurs [10], about $\lambda = 0.8$.

We define in section 4 two effective Hamiltonians which shift all unphysical state energies up into the physical continuum without altering the physical, bound state energies or wave functions. Our objective is to see if the polarization approximation can be saved by changing the Hamiltonian. It is worth saving because it is a simple approximation and because it gives the asymptotic $1/R$ expansion coefficients correctly [2,9]. We show that the perturbation theories based on these effective Hamiltonians are unsatisfactory as new bases for the theory of intermolecular interactions. The ways in which they are unsatisfactory are similar, suggesting that a more sophisticated approach might be successful.

The Hirschfelder–Silbey (HS) method is more sophisticated than the polarization approximation and, like the latter, gives correctly the leading terms in the asymptotic $1/R$ expansion in the second order in the energy [10–12]. Unfortunately, the HS method may also diverge due to the unphysical states. In section 5, we review the theoretical basis for the HS method, then develop three new HS Hamiltonians based on the two effective Hamiltonians introduced in section 4. We show that two fail certain tests and must be classed as unacceptable. The third passes these tests, but it will require further study to determine if it solves the unphysical-states problem for the HS method.

In the last section, we put into perspective what we have learned in this paper. Our attempts to design an effective Hamiltonian which gets around the unphysical-states problem appear to have been successful, but it was not the straightforward process the word "design" suggests.

2. Configuration interaction calculations on LiH

The results we derived previously [3] for LiH at infinite R show that it is unlikely that the lowest energy eigenfunction of $\hat{H}^0$ is transformed by the perturbation $\hat{V}$ into the lowest energy physical eigenfunction of $\hat{H} = \hat{H}^0 + \hat{V}$. How the eigenvalues of $\hat{H}^0 + \lambda\hat{V}$ at finite R change as λ increases from 0 to 1 was left to conjecture. In fact, one might hope that our discussion, or even Claverie's analysis [1] of the He_2 interaction, omits some important point that will somehow make the polarization approximation work correctly in the end. Here, we show by ab initio calculations that the lowest energy eigenstate of $\hat{H}^0$ smoothly becomes the lowest energy, unphysical eigenstate of $\hat{H}$ as λ increases from 0 to 1. The calculations have been carried out with an unconventional configuration interaction [CI] program, one in which each configuration is a product of two determinants.

Before we can discuss our numerical results, we have to explain the ideas on which the program is based and what one can expect to learn from it. We begin by dividing the N electrons of a diatomic molecule between the two atoms, A and B, assigning electrons $1, 2, \ldots, N_A$ to A, and the rest to B. Let $\hat{h}_A$ be the nonrelativistic Hamiltonian of A in the absence of B, and define $\hat{h}_B$ analogously. The perturbing potential $\hat{V}$ is just the difference between $\hat{H}$, the nonrelativistic Hamiltonian for the molecule in the Born–Oppenheimer approximation, and $\hat{H}^0 = \hat{h}_A + \hat{h}_B$, i.e., $\hat{V} = \hat{H} - \hat{H}^0$. Note that the operators which interchange A-atom electrons among themselves commute with $\hat{H}^0$ and $\hat{V}$. The same is true for the operators which interchange the B-atom electrons. Thus, we can require that the eigenfunctions $\Psi(\lambda)$ of $\hat{H}^0 + \lambda\hat{V}$ be antisymmetric under single interchanges of A-atom electrons and, separately, under interchanges of B-atom electrons. This limits in no way the generality of our analysis since we are interested in the interactions between atoms which are in states satisfying the Pauli principle. The $\Psi(\lambda)$ will generally have no particular symmetry under the interchange of an A-atom electron with a B-atom electron when $\lambda \neq 1$. Thus, we can expand $\Psi(\lambda)$ in a basis set of functions, each of which is antisymmetric in electron coordinates 1 through N_A and, separately, in coordinates $N_A + 1$ through N. We have used a *bideterminantal* basis, i.e., one in which each basis function is the product of two Slater determinants, one for the first N_A electrons and one for the remaining N_B electrons. The same set of orthonormalized, basis orbitals has been used in constructing both the A and B determinants.

The reader might remark at this point that the interchange of electron 1 from the A-determinant with electron N from the B-determinant, for example, gives a function which is neither antisymmetric under interchanges of coordinate 1 with other A-group coordinates, nor antisymmetric under interchanges of coordinate N

with other B-group coordinates. In other words, the bideterminantal basis does not provide a representation of all single-interchange operators. In our earlier discussion [3] of the states of LiH, we implicitly used a bideterminantal basis, but we failed to discuss this aspect carefully, with the consequence that there is an error in fig. 2 of that paper.

Although the bideterminantal basis does not provide a representation of the single-interchange operators $\hat{\mathcal{P}}_{ij}$, it does provide a representation of the operator $\hat{\mathcal{P}}_{ij} = \sum_{i\in A}\sum_{j\in B}\mathcal{P}_{ij}$, i.e. i is summed over A-atom coordinates, j over B-atom coordinates. The demonstration of this for LiH is straightforward. Although it is irrelevant to our discussion of LiH, it is worth remarking here that the bideterminantal basis also provides a representation of the operator which is a sum over all double interchanges of coordinates between groups, the operator which is a sum over all triple interchanges, and so on. In view of this limitation of the bideterminantal basis, fig. 2 in our previous paper [3] incorrectly shows that each of the two lowest eigenstates of $\hat{H}^0$ for LiH correlate with four eigenstates of $\hat{H}$, one physical and three unphysical. In fact, in the bideterminantal basis, each of the eigenstates of $\hat{H}^0$ for LiH correlates with one physical and one unphysical state of $\hat{H}$. At infinite R, the physical function is obtained from the $\hat{H}^0$ eigenfunction F_k^0 by application of $1-\hat{\mathcal{P}}_I$, the unphysical, by application of $3+\hat{\mathcal{P}}_I$. That there is only a doubling of each $\hat{H}^0$ state is consistent with our numerical results. See the appendix for details.

In constructing the orbital basis set for the calculations reported here, we have used the Hartree–Fock 1s, 2s and 2pσ orbitals of Li, and the 1s, 2s and 2pσ hydrogen atom orbitals. These are sufficient to give a Hartree–Fock level of accuracy for the two lowest energy levels of each atom at infinite R. The Hartree–Fock orbitals of Li were expanded in an STO basis. These six atomic orbitals were transformed into an orthonormal set by Löwdin's method [13] because we wanted to work with an atomic-like set of orthonormal basis orbitals. This gave a total of 1080 bideterminantal configurations for the full CI calculations on singlet states. Integrals were evaluated using the BISON program [14].

In fig. 1, we present our results for the lowest energy, $^1\Sigma$ levels of $\hat{H}^0+\lambda\hat{V}$ for LiH at $R = 5.0$ Bohr. Note that we have included the nuclear–nuclear repulsion term in $\hat{V}$. At $\lambda = 1$, five unphysical states appear below the lowest energy, physical state. One can clearly see from fig. 1 that the lowest energy physical state begins at $\lambda = 0$ as the sixth lowest eigenstate of $\hat{H}^0$. This $E(\lambda)$ is involved in six avoided crossings between $\lambda = 0$ and $\lambda = 1$, the last occurring at $\lambda = 1$. The lowest energy eigenstate of $\hat{H}^0$ is transformed by the interaction into the lowest energy unphysical state of $\hat{H}^0+\hat{V}$.

In fig. 2, we have replotted the data from fig. 1 on a larger scale so that some of the avoided crossings can be seen in more detail. This should leave little doubt that the lowest eigenvalue $E_1(\lambda)$ of $\hat{H}^0+\lambda\hat{V}$ is a continuous function of λ, and that the expansion of $E_1(\lambda)$ in powers of λ can not converge at $\lambda = 1$ to the energy of the physical ground state. In fact, we show in the next section that the expansion

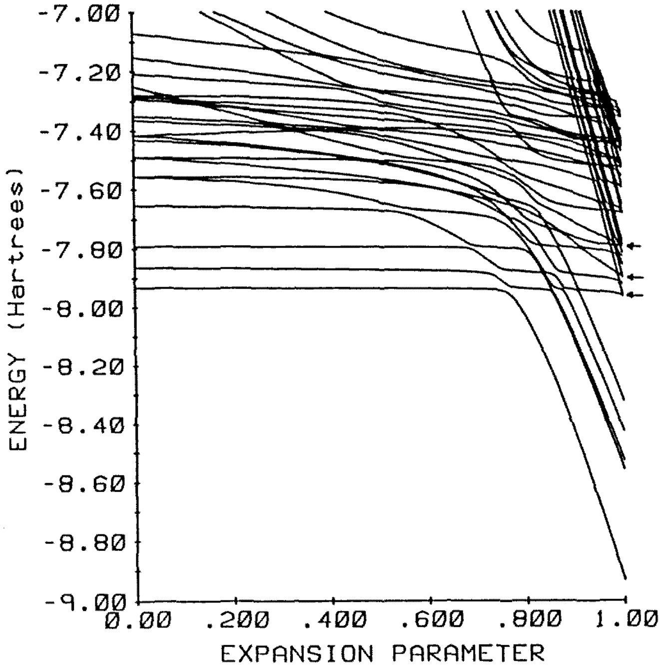

Fig. 1. The eigenvalues of $\hat{H}^0 + \lambda\hat{V}$ for $^1\Sigma$ states of LiH at $R = 5.0$ Bohr plotted against the expansion parameter λ. The locations of the three lowest energy physical states at $\lambda = 1$ are marked by arrows.

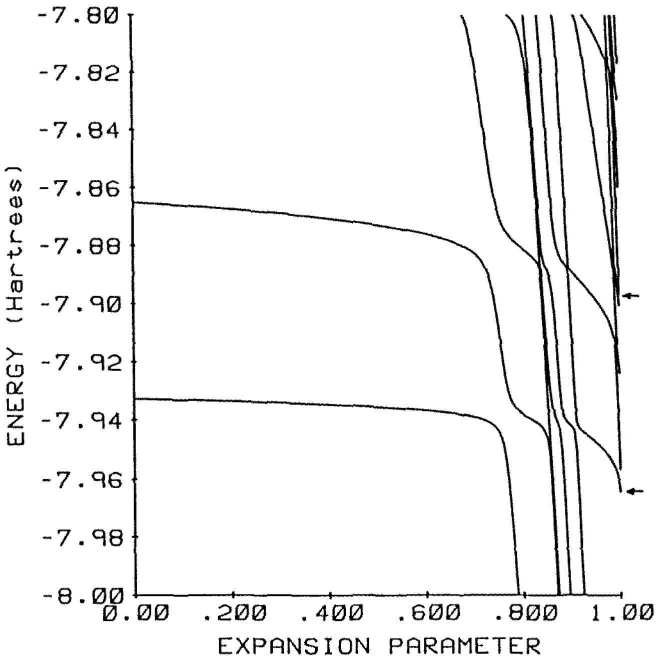

Fig. 2. The eigenvalue data of fig. 1 replotted using a finer energy scale so that the avoided crossings are clearly seen. The locations of the two lowest energy physical states are indicated by arrows.

must diverge for λ greater than the value of λ at which the first avoided crossing occurs.

In fig. 3, we have plotted the values of $E_k(\lambda)$ for LiH at 10.0 Bohr. Note that it is not clear from this figure that avoided crossings have occurred, although this can be verified by replotting the data on the same scale used in fig. 2. Figure 3 makes it look like the lowest eigenvalue at $\lambda = 0$ crosses several other eigenvalues as λ increases, becoming at $\lambda = 1$ the energy of the physical ground state. In fact, what one is seeing for $k = 1$ to 5 is the λ dependence of $E_k(\lambda)$ before the avoided crossing, continuing in the λ dependence of $E_{k+1}(\lambda)$ after the avoided crossing. We show in section 3 that this is just the type of behavior one expects to see when two states interact weakly. It is this behavior that probably explains why the coefficients in the asymptotic $1/R$ expansion can be determined exactly by the polarization approximation. On the other hand, one must remember that if we could do exact calculations of the $E_k(\lambda)$ for LiH, we would see an infinite number of discrete energies below the physical ground-state energy and a continuum of energies overlaying it. Thus, we expect the $E_k(\lambda)$, which becomes the physical ground-state energy at $\lambda = 1$, to be involved in an infinite number of avoided crossings, the cumulative effect of which is difficult to project.

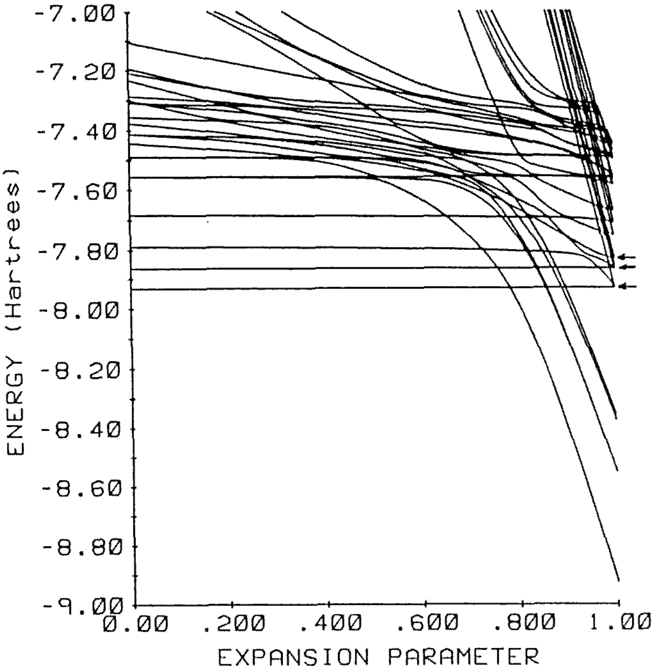

Fig. 3. The eigenvalues of $\hat{H}^0 + \lambda\hat{V}$ for ${}^1\Sigma$ states of LiH at $R = 10.0$ Bohr plotted against the expansion parameter λ. The locations of the three lowest energy physical states at $\lambda = 1$ are marked by arrows.

Our ab initio calculations show that the problem first recognized by Claverie [1], and Morgan and Simon [2], is real. They also show that our analysis [3] of the LiH system at infinite R did not overstate the seriousness of the problem. We find it difficult to see how a mathematically correct theory of intermolecular interactions at finite R, perturbative or nonperturbative, can be developed by ignoring it.

3. Persistence of eigenvalue trends through avoided crossings

Figure 3 clearly exhibits what can be described as the persistence of eigenvalue trends through avoided crossings. One can easily understand why the trends persist by looking at a two-state problem. The two-state problem also shows that the radius of convergence of the perturbation expansion in powers of λ must be less than the value of λ at which the first avoided crossing occurs. This point has already been made by Kutzelnigg [10] in a detailed study of the limiting processes used in intermolecular perturbation theory.

Let χ_1 and χ_2 be the two state functions which interact. We set

$$H_{kk} = \langle \chi_k | \hat{H}^0 + \lambda \hat{V} | \chi_k \rangle = \varepsilon_k + \lambda V_{kk}$$

and

$$H_{12} = \langle \chi_1 | \hat{H}^0 + \lambda \hat{V} | \chi_2 \rangle = \lambda V_{12} .$$

Note that for the last equality to hold we must assume that either χ_1 or χ_2 is an eigenfunction of $\hat{H}^0$, and that χ_1 is orthogonal to χ_2. We could drop the requirement of orthogonality, but it gains us nothing and makes the analysis more complicated. The solution of the two-state secular equation is

$$E_\pm = \tfrac{1}{2}(H_{11} + H_{22}) \pm \tfrac{1}{2}\sqrt{(H_{22} - H_{11})^2 + 4H_{12}^2} . \tag{3.1}$$

We assume that $\varepsilon_2 > \varepsilon_1$, so that for λ small enough, $H_{22} > H_{11}$. In order to have an avoided crossing, we must have $\varepsilon_2 + V_{22} < \varepsilon_1 + V_{11}$, i.e., for λ close to 1, $H_{22} < H_{11}$. Let λ_c be the value of λ at which $H_{22} = H_{11}$, i.e., $\lambda_c = (\varepsilon_2 - \varepsilon_1)/(V_{11} - V_{22})$.

The key expression for understanding the behavior immediately before and after the avoided crossing is derived from eq. (3.1). For values of λ smaller than λ_c, if V_{12} is sufficiently small, we can expand the radical in eq. (3.1) in powers of $H_{12}^2/(H_{22} - H_{11})^2$. For $\lambda < \lambda_c$, the difference $H_{22} - H_{11}$ is positive, so that

$$E_+ = \varepsilon_2 + \lambda V_{22} + \frac{\lambda^2 V_{12}^2}{\varepsilon_2 - \varepsilon_1 + \lambda (V_{22} - V_{11})} + \dots , \tag{3.2}$$

$$E_- = \varepsilon_1 + \lambda V_{11} - \frac{\lambda^2 V_{12}^2}{\varepsilon_2 - \varepsilon_1 + \lambda (V_{22} - V_{11})} + \dots . \tag{3.3}$$

For $\lambda > \lambda_c$, on the other hand, $H_{22} - H_{11}$ is negative, so that the expression for E_+ then is identical to the expression on the right-hand side in eq. (3.3), and that for E_-, to the one on the right-hand side in (3.2). In short, as λ increases through λ_c, the formula for the upper energy state becomes the formula for the lower state, and vice versa. Since V_{12} has been assumed to be very small in magnitude, the term linear in λ in E_+ and E_- dominates the behavior of the eigenvalues before and after the avoided crossing, hence the persistence of the eigenvalue trends as functions of λ. One can also readily verify that after the avoided crossing, the upper energy state function is predominantly χ_1, the lower χ_2, i.e., exactly the opposite of the situation for $\lambda < \lambda_c$.

We have expanded the energy expression (3.1) in a power series, but not in powers of λ as is done in the polarization approximation. The radius of convergence of the λ expansion is determined by the condition $(H_{22} - H_{11})^2 + 4H_{12}^2 = 0$. This implies convergence for real $\lambda < \lambda_c/\sqrt{K}$ with $K = 1 + 4|V_{12}|^2/(V_{11} - V_{22})^2$. Since we have assumed here that $|V_{12}| \ll V_{11} - V_{22}$, the radius of convergence is only slightly smaller than λ_c.

It is instructive to look more closely at the first avoided crossing undergone by the lowest energy state in fig. 3 from the standpoint of the two-state model. We know that χ_1, for sufficiently large R, is the singlet projection of the antisymmetrized product of the Li ground-state wave function for electrons 1–3 with the hydrogen 1s for electron 4. The function χ_2 is more complicated to define. We know that after the crossing, the lowest energy function must be predominantly χ_2, and that this function must be the lowest energy unphysical state function of LiH. We discussed this function extensively in our previous paper [3]. Here, it should be enough to describe how to construct it from the lowest energy doublet, unphysical wave function of Li, the one which can be described loosely as a $1s^3$ configuration, and the hydrogen 1s function. We assign electron coordinates 1 and 2 of Li, and 4 of H, to the unphysical Li function, and coordinate 3, that of an Li electron, to the hydrogen 1s orbital. We must require that the Li function be antisymmetric in coordinates 1 and 2 so that χ_2 can be antisymmetric in the Li electronic coordinates 1, 2 and 3, as we have assumed. The product of the Li function and the hydrogen spin–orbital, spin projected and made antisymmetric in coordinates 1, 2 and 3, is χ_2. Because χ_2 puts the hydrogen electron coordinate 4 in the Li function, and one Li coordinate in the hydrogen function, V_{12} and $\langle\chi_2|\chi_1\rangle$ must, like overlap integrals, decrease exponentially with increasing R. Since each of the unphysical states of LiH which lie below its physical ground state puts the hydrogen electron in the Li function [3], the matrix element V_{12} for each isolated avoided crossing of a physical and unphysical LiH function will be a function of $\exp(-R)$. This should help to explain why the polarization approximation gives the asymptotic $1/R$ dependence of the energy correctly.

Consider the matrix elements $H_{kl} = \langle\chi_k|\hat{H}^0 + \lambda\hat{V}|\chi_l\rangle$, where both χ_k and χ_l are products of a physical eigenfunction of Li and a hydrogen orbital. For $k \neq l$ and R very large, these matrix elements can be expanded in positive powers of $1/R$ just as they were in Ahlrichs' work on the asymptotic $1/R$ expansion [9]. Comparing this to the $\exp(-R)$ dependence of matrix elements between physical and unphysical states found in the preceding paragraph, we conclude that one must be able to calculate the coefficients of the asymptotic $1/R$ expansion correctly using the polarization approximation, because the interaction matrix elements between unphysical and physical states vanish so quickly with increasing R compared to the way matrix elements between physical states vanish.

We find it interesting that our calculations show that the physical ground state is involved in a final avoided crossing at $\lambda = 1$. It is interesting in part because it is the avoided crossing that the Heitler–London method takes into account. It is also interesting because the state that becomes the physical ground state at $\lambda = 1$ must be involved as well in avoided crossings with the continuum of unphysical states as λ approaches 1. We do not know what the total effect of these avoided crossings might be.

The avoided crossings depicted in figs. 1–3 are more complicated than those of the two-state model, but the two-state model is sufficient for understanding the persistence shown in the trends of the $E_k(\lambda)$ through avoided crossings. It also gives an insight into how the polarization approximation can give the asymptotic $1/R$ dependence of the energy correctly in spite of the many avoided crossings with unphysical states.

4. Polarization approximation with energy level shifting

Since we know that the unphysical eigenstates of $\hat{H}$ are a definite barrier to the construction of a convergent perturbation theory of intermolecular interactions, one would think that if we could replace the actual molecular Hamiltonian $\hat{H}$ by an effective Hamiltonian $\hat{\mathcal{H}}_e$, which has the same eigenfunctions at $\hat{H}$ but which shifts all of the unphysical energies up into the physical continuum, the unphysical states problem would disappear. In this section, we define two such effective Hamiltonians and attempt to develop from them perturbation methods in the same direct and obvious way in which the polarization approximation was developed. The exercise is instructive but bears no immediate fruit.

In a sense, what we are trying to do in this section is to save the polarization approximation. The polarization approximation has the attractive property that its second-order energy gives exactly the coefficients of the leading terms in the asymptotic $1/R$ expansion [2,9]. To calculate anything other than these coefficients with the polarization approximation, however, is of questionable validity given the difficulties noted by Claverie [1], and Morgan and Simon [2], and the results presented in section 2 of this paper. In contrast to the polarization approximation, the perturbation theories that have no unphysical-states problem for the ground state [5,7,8] have been found in calculations on H_2 to give only a fraction of the coefficients of the leading terms in second order [11,15].* Thus, there is a need for a better perturbation theory.

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*The calculations in [15] correct some errors in the results in [11].

4.1. SIMPLE SHIFTING OF THE UNPHYSICAL STATES

The simplest effective Hamiltonian, which has both the physical eigenfunctions Φ_k and the unphysical eigenfunctions u_k of $\hat{H}$ as its eigenfunctions, is $\hat{\mathcal{H}}_e = \hat{H} + B(1 - \hat{\mathcal{A}})$, in which B is a positive number and $\hat{\mathcal{A}}$ is the projection operator onto the space of functions which are totally antisymmetric in the electronic position and spin coordinates. Note that $\hat{\mathcal{A}}\Phi_k = \Phi_k$ and $\hat{\mathcal{A}}u_k = 0$. The physical energies E_k are eigenstates of both $\hat{H}$ and $\hat{\mathcal{H}}_e$. The eigenenergies of the unphysical states are E_k^u with $\hat{H}$, but $E_k^u + B$ with $\hat{\mathcal{H}}_e$. By choosing B large enough, one can shift all of the unphysical eigenstate energies so that they are higher than the energies of all of the bound, physical, electronic states of the system. It appears that it is easy to eliminate the avoided crossings that invalidate the polarization approximation.

In the polarization approximation, it is assumed that the unperturbed Hamiltonian $\hat{H}^0$is the sum of atomic Hamiltonians, and that the perturbation is $\hat{V} = \hat{H} - \hat{H}^0$. We make the same division in $\hat{\mathcal{H}}_e$ so that the unperturbed problem is $\hat{H}^0 F^0 = \varepsilon^0 F^0$, where F^0 is a spin-projected product of an A-atom eigenfunction and a B-atom eigenfunction. The perturbation is $\hat{V} + B(1 - \hat{\mathcal{A}})$, which gives for the first-order energy $E^{(1)} = \langle F^0 | \hat{V} | F^0 \rangle + B \langle F^0 | 1 - \hat{\mathcal{A}} | F^0 \rangle$. We know that as R tends to infinity, $\langle F^0 | \hat{V} | F^0 \rangle$, the first-order energy of the polarization approximation, approaches zero. This is consistent with the idea that the perturbation corrections correspond to contributions to the interatomic potential. For this reason, it is unsatisfactory that $E^{(1)}$ does not approach zero as R becomes infinite. As R becomes infinite, $\langle F^0 | 1 - \hat{\mathcal{A}} | F^0 \rangle$ approaches the limit $1 - N_A! N_B! / N!$ if F^0 is normalized. This is because $\langle F^0 | \hat{\mathcal{P}}_{ij} | F^0 \rangle = 0$ in the limit of $R = \infty$ when $\hat{\mathcal{P}}_{ij}$ exchanges an A-atom electron with a B-atom electron. This result for $E^{(1)}$ is not surprising since F^0 is not an eigenfunction of $\hat{\mathcal{H}}_e$ at infinite separation, although the function $\hat{\mathcal{A}}F^0$ is. Thus, at infinite R, the perturbation expansion must change F^0 into $\hat{\mathcal{A}}F^0$, which is not a small change.

It may be that the undesirable properties of the perturbation method outlined in the preceding paragraph are a consequence of choosing the unperturbed problem badly. We could have chosen $\hat{H}^0 + B(1 - \hat{\mathcal{A}})$ as the unperturbed Hamiltonian instead of $\hat{H}^0$. This choice has a major drawback: neither F^0 nor $\hat{\mathcal{A}}F^0$ is one of its eigenfunctions, even at infinite R. This is sufficient reason for not considering it further.

If, because the avoided crossings between discrete physical states and the unphysical states have been eliminated, one chooses to ignore the obvious problems of the first perturbation method, the one based on $\hat{H}^0$ as the unperturbed Hamiltonian, we have to recognize that there is no assurance that the perturbation expansion will converge in any useful sense. Again it is helpful to look at the infinite R limit. We know that $\hat{\mathcal{A}}F^0$ is an eigenfunction of $\hat{\mathcal{H}}_e$ in that limit. The overlap between $\hat{\mathcal{A}}F^0$, when normalized, and the unperturbed function F^0 approaches the limit $\sqrt{(N_A! N_B! / N!)}$. For LiH, the limit is 1/2, for Ne_2, 2.33×10^{-3}. The larger N is, the bigger the correction to be determined by the perturbation summation. We do not regard this as acceptable.

4.2. SHIFTING AND TRANSFORMING THE UNPHYSICAL STATES

That the effective Hamiltonian with simple shifting of the unphysical energies does not lead to a useful perturbation theory is not disappointing to us because we do not like the arbitrary parameters like B. In this subsection, we analyze an alternative effective Hamiltonian, one without adjustable parameters. To define it, we use $\hat{\mathcal{A}}$ and the operators which appear in the molecular Hamiltonian $\hat{H}$, namely, the total kinetic energy operator $\hat{t}$, the total nuclear–electron potential operator $\hat{v}$, and the total electron–electron repulsion operator $\hat{g}$. Let $\hat{\mathcal{H}}_\mathrm{e} = \hat{t} + \hat{v}\hat{\mathcal{A}} + \hat{g}$. Note that $\hat{\mathcal{H}}_\mathrm{e}$ is Hermitian because $\hat{\mathcal{A}}$ and $\hat{v}$ commute. This definition was inspired by the one-electron Hamiltonian of Mann and Privman [16], and by Hirschfelder's version [5] of the Eisenschitz–London perturbation theory.

The physical eigenfunctions of $\hat{\mathcal{H}}_\mathrm{e}$ are the Φ_k and their eigenvalues are the corresponding E_k. Since $\hat{\mathcal{A}}\Phi_k = \Phi_k$, one can see immediately that $\hat{\mathcal{H}}_\mathrm{e}\Phi_k = \hat{H}\Phi_k = E_k\Phi_k$, as stated. Since the physical eigenfunctions are orthogonal to the unphysical functions, $\langle u_j | \hat{\mathcal{H}}_\mathrm{e} | \Phi_k \rangle = 0$, and the effective Hamiltonian does not mix the physical and unphysical states. The unphysical functions, however, are not eigenfunctions of $\hat{\mathcal{H}}_\mathrm{e}$. Since $\hat{\mathcal{A}}u_k = 0$, one sees that $\hat{\mathcal{H}}_\mathrm{e}u_k = (\hat{t} + \hat{g})u_k$; the unphysical eigenfunctions of $\hat{\mathcal{H}}_\mathrm{e}$ must be mixtures of the u_k. Since $\hat{t} + \hat{v}$ is a positive definite operator, the unphysical eigenvalues of $\hat{\mathcal{H}}_\mathrm{e}$ must all be positive. This means that $\hat{\mathcal{H}}_\mathrm{e}$ shifts the energies of the unphysical states well up into the physical continuum. The unphysical states are exactly those of a very low density, free-electron gas.

It is convenient, in basing a perturbation method on this effective Hamiltonian, to rewrite $\hat{\mathcal{H}}_\mathrm{e}$ in the form $\hat{\mathcal{H}}_\mathrm{e} = \hat{H} - (1 - \hat{\mathcal{A}})\hat{v}$. As in the preceding subsection, we first choose $\hat{H}^0$ as the unperturbed Hamiltonian, and write F^0 for its eigenfunction. The perturbation is $\hat{V} - (1 - \hat{\mathcal{A}})\hat{v}$. The first-order energy is $E^{(1)} = \langle F^0 | \hat{V} | F^0 \rangle - \langle F^0 | (1 - \hat{\mathcal{A}})\hat{v} | F^0 \rangle$. In the limit of infinite R, this first-order energy approaches the limit $(1 - N_\mathrm{A}!N_\mathrm{B}!/N!)\langle F^0 | \hat{v} | F^0 \rangle$, which is not zero. In fact, it is quite large because $\langle F^0 | \hat{v} | F^0 \rangle$ is the expectation value of the nuclear–electron potential energy for A plus that of B. As above, it is not acceptable to have $E^{(1)}$ approach a nonzero limit at infinite separation. If we choose the unperturbed Hamiltonian to be $\hat{H}^0 - (1 - \hat{\mathcal{A}})\hat{v}$, then neither F^0 nor $\hat{\mathcal{A}}F^0$ are eigenfunctions, which is also unacceptable.

In spite of the above drawbacks, one could choose to use this $\hat{\mathcal{H}}_\mathrm{e}$ anyway. One can verify that $\hat{\mathcal{A}}F^0$ is an eigenfunction of $\hat{\mathcal{H}}_\mathrm{e}$ in the $R = \infty$ limit. This implies, by the line of reasoning used in the preceding subsection, that F^0 will generally have small overlap with the exact eigenfunction of $\hat{\mathcal{H}}_\mathrm{e}$ and that the perturbation correction will be correspondingly large. In short, this effective Hamiltonian has the same shortcomings as that in the preceding subsection.

Although our examination of two effective Hamiltonians can not be called an exhaustive search for an improved starting point for the polarization approximation, it does serve to clarify the nature of the problem. We believe it is significant that the shortcomings of the two effective Hamiltonians are basically the same. Clearly, there is more to getting around the unphysical-states problem than shifting the unphysical states up in energy so that their spectrum no longer begins below the physical-states spectrum.

5. Hirschfelder–Silbey method revisited

The Hirschfelder–Silbey (HS) perturbation method has the attractive feature that its second-order energy gives correctly the coefficients of the leading terms in the asymptotic $1/R$ expansion of the energy of interacting atoms and molecules [10]. Unfortunately, the HS method has one of the same defects as the polarization approximation: the spectrum of the HS effective Hamiltonian differs minimally from that of $\hat{H}$, so that even the lowest eigenvalue of the HS Hamiltonian for a physical solution is higher in energy than an infinite number of unphysical, discrete solutions, and is buried in a continuum of energies of unphysical, unbound solutions [3]. We write here physical and unphysical solutions rather than states, because the HS eigenfunctions that we want to calculate are not eigenfunctions of $\hat{H}$, only their projections onto irreducible representations of the symmetric group are. By a physical solution of the HS equation, we mean one which has a nonzero, antisymmetric projection, by an unphysical one, one which does not. In this section, we consider if the HS method can be modified in a way that gets around the unphysical-states problem.

The HS method is based on the idea of exploiting exchange symmetry to define a function F which differs minimally from F^0 in some sense. The original formulation [4,5] implicitly defines F in terms of the perturbation equations, not by some independent criterion. It is assumed that F can be written as a linear combination of a finite number of $\hat{H}$ eigenfunctions, one physical and the rest unphysical. Each eigenfunction used is assumed to have the same asymptotic $1/R$ expansion, and no two are assumed to belong to the same irreducible representation of the symmetric group unless they belong to different rows.

The version of the HS method due to Polymeropoulos and Adams [5] is less specific about which functions are combined in F, but it does give an effective Hamiltonian $\hat{\mathcal{H}}_{\mathrm{H}}$. It is this Hamiltonian which we have analyzed [3] and which is called the HS Hamiltonian in the remainder of this paper. In the following subsection, we review the Polymeropoulos–Adams formulation in preparation for considering how it may be modified to remove the problems caused by unphysical states.

5.1. THE HS EFFECTIVE HAMILTONIAN AND THE LEAST DISTORTION CRITERION

To understand how to improve the HS method, one has to understand how the properties of the HS effective Hamiltonian have been established. The best way to explain this should be to go through the derivation in the present context. What follows should be clearer than the original discussion [17].

In this paper, we have so far considered only one partition of the electrons between the two interacting atoms or molecules: the one which assigns electrons $1, \ldots, N_A$ to A and electrons $N_A + 1, \ldots, N = N_A + N_B$ to B. This is just one of $N!/(N_A!N_B!)$ possible partitions. We can obtain any one of these partitions from the first by interchanging pairs of electrons between the atoms. Let $\hat{\mathcal{P}}_r$ be the operator which produces the rth partition from the first. We write $\hat{\mathcal{P}}_1$ for the identity operator. Instead of simply using $\hat{H}^0$ and $\hat{V}$ for the operators corresponding to the first partition, we now write $\hat{H}_1^0$ and $\hat{V}_1$, and instead of F^0 for the eigenfunction of $\hat{H}_1^0$, we use F_1^0. We define $F_r^0 = \hat{\mathcal{P}}_r F_1^0$, $\hat{H}_r^0 = \hat{\mathcal{P}}_r \hat{H}_1^0 \hat{\mathcal{P}}_r^{-1}$ and $\hat{V}_r = \hat{\mathcal{P}}_r \hat{V}_1 \hat{\mathcal{P}}_r^{-1}$. It follows from $\hat{H}_1^0 F_1^0 = \varepsilon^0 F_1^0$ that $\hat{H}_r^0 F_r^0 = \varepsilon^0 F_r^0$.

Let F_1 be a function of the N electronic position-spin coordinates which, like F_1^0, is antisymmetric in coordinates $1, \ldots, N_A$ and, separately, in coordinates $N_A + 1, \ldots, N$. Later we explain the sense in which F_1 is least distorted from F_1^0, but for the moment it is enough to think of it as a function approximately like F_1^0. Let $F_r = \hat{\mathcal{P}}_r F_1$. We assume that the functions F_r which result from operating on F_1 with all of the distinct $\hat{\mathcal{P}}_r$ form a linearly independent set, which we call the HS set. We form from the N-electron overlap integrals $S_{rs} = \langle F_r | F_s \rangle$ calculated between all members of the HS set the matrix S. Since the functions in the HS set are assumed to be linearly independent, the inverse of S exists. The elements of the inverse of S are D_{rs}.

We define the HS effective Hamiltonian by

$$\hat{\mathcal{H}}_{11} = \hat{H}_1^0 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q},$$

with

$$\hat{Q} = \sum_{r,s} |F_r\rangle D_{rs} \langle F_s|. \tag{5.1}$$

The sum extends over all functions in the HS set. It follows from (5.1) that $\hat{Q}$ is a projection operator, i.e., $\hat{Q}$ is Hermitian, $\hat{Q}^2 = \hat{Q}$, and the trace of $\hat{Q}$ equals an integer, the number of functions in the HS set. Another important property of $\hat{Q}$ is that $\hat{\mathcal{P}}_r \hat{Q} = \hat{Q}\,\hat{\mathcal{P}}_r$. One can prove this starting from the observation that $\hat{\mathcal{P}}_r F_s$ must be another function in the HS set.

THEOREM

If F_1 satisfies

$$\hat{\mathcal{H}}_{11} F_1 = \varepsilon F_1, \tag{5.2}$$

where ε is a constant, and $\hat{\mathcal{H}}_{11}$ and $\hat{Q}$ are defined by (5.1), then $\hat{\mathcal{A}} F_1$, if it does not vanish identically, is an eigenfunction of $\hat{H} = \hat{H}_1^0 + \hat{V}_1$, the eigenvalue being

$$E = \varepsilon + \frac{\langle F_1 | \hat{\mathcal{A}} \hat{V}_1 | F_1 \rangle}{\langle F_1 | \hat{\mathcal{A}} | F_1 \rangle}. \tag{5.3}$$

The proof is brief. Since $\hat{\mathcal{P}}_r$ and $\hat{Q}$ commute, $\hat{Q}$ can be expressed in terms of functions which belong to irreducible representations of the group formed by the set of $\hat{\mathcal{P}}_r$. In particular, one contribution to $\hat{Q}$ must be $\hat{\mathcal{A}}|F_1\rangle(\langle F_1|\hat{\mathcal{A}}|F_1\rangle)^{-1}\langle F_1|\hat{\mathcal{A}}$. If one operates on eq. (5.2) from the left with $\hat{\mathcal{A}}$, and at the same time uses the identity $\hat{Q}F_1 = F_1$, one obtains

$$\hat{\mathcal{A}}\hat{H}F_1 - \hat{\mathcal{A}}F_1 \frac{\langle F_1|\hat{\mathcal{A}}\hat{V}_1|F_1\rangle}{\langle F_1|\hat{\mathcal{A}}|F_1\rangle} = \varepsilon\,\hat{\mathcal{A}}F_1 .$$

Since $\hat{H}$ commutes with all of the $\hat{\mathcal{P}}_r$, it must commute with $\hat{\mathcal{A}}$, too. The theorem is proved. Note that the eigenvalue expression (5.3) has the same form as the energy formula in the Heitler–London approximation and that it may be interpreted in a similar way [18]. Equation (5.3) is only one of several formulas for E that can be used in the derivation of a perturbation expansion [6].

There are other consequences of the above equations. From the definition of $\hat{Q}$, it follows that $\hat{Q}F_r = F_r$. This allows us to rewrite (5.2) in the form $[\hat{H}_1^0 + (1-\hat{Q})\hat{V}_1]F_1 = \varepsilon F_1$. Because $\hat{\mathcal{P}}_r$ and $\hat{Q}$ commute, this equation implies that

$$[\hat{H}_r^0 + (1-\hat{Q})\hat{V}_r]F_r = \varepsilon F_r . \tag{5.4}$$

If we multiply (5.4) from the left by $1-\hat{Q}$, and use the projection operator property of $\hat{Q}$, we obtain $(1-\hat{Q})(\hat{H}_r^0 + \hat{V}_r)F_r = (1-\hat{Q})\hat{H}F_r = 0$ for all r, since the sum of $\hat{H}_r^0$ and $\hat{V}_r$ is exactly $\hat{H}$. Because $(1-\hat{Q})\hat{H}F_r = 0$ for all r, it must be true that $(1-\hat{Q})\hat{H}\hat{Q} = 0$, from which one can immediately prove that $\hat{H}$ and $\hat{Q}$ commute. This means that $\hat{Q}$ must be equal to $|\Phi_1\rangle\langle\Phi_1| + \sum_k |u_k\rangle\langle u_k|$ if $\hat{\mathcal{A}}F_1 \propto \Phi_1$, the lowest energy physical eigenfunction of $\hat{H}$. The sum is over a finite number of the unphysical eigenfunctions u_k of $\hat{H}$ because the trace of $\hat{Q}$ is a finite integer.

To develop a perturbation theory from the above results, we inserted λ in front of $\hat{V}_1$ in eq. (5.2) and expanded F_1, ε and $\hat{Q}$ in power series λ [6]. If $\hat{Q}(\lambda)$ could be expressed exactly in terms of some eigenfunctions of $\hat{H}_1^0 + \lambda\hat{V}_1$, as we have just established that it can be for $\lambda = 1$, then the results of the calculations discussed in section 2 could be applied to the HS perturbation method. This is not the case. We can insert λ in front of $\hat{V}_1$ in eq. (5.1), proceed through (5.2) to derive eq. (5.4) and deduce, since $\hat{Q}(\lambda)$ must still be a projection operator, that $(1-\hat{Q}(\lambda))(\hat{H}_r^0 + \lambda\hat{V}_r)F_r(\lambda) = 0$ for all r. Since $\hat{H}_r^0 + \lambda\hat{V}_r \neq \hat{H}_s^0 + \lambda\hat{V}_s$ for $\lambda < 1$ and $r \neq s$, the argument that was used in the preceding paragraph can not be used here. The operator $\hat{Q}(\lambda)$ does not commute with $\hat{H}_1^0 + \lambda\hat{V}_1$ and $\hat{Q}(\lambda)$ can not be expressed in terms of a finite number of the eigenfunctions of $\hat{H}_1^0 + \lambda\hat{V}_1$ for $\lambda < 1$.

We have asserted above that F_1 is related to F_1^0 in some way. In the limit $\lambda = 1$, we have shown that $\hat{Q}$ can be expressed in terms of one physical eigenfunction of $\hat{H}$ and a finite number of the unphysical eigenfunctions. Since $\hat{Q}F_1 = F_1$, we can set $F_1 = C_0\Phi_1 + \sum_k c_k u_k$, the sum being over the u_k which contribute to $\hat{Q}$. The coefficients C_0 and c_k are fixed by eq. (5.2) but, for the moment, we regard them as parameters which we can adjust in any way we like. Let us choose these coefficients so that F_1 is least distorted from F_1^0 in the sense that $\langle F_1|\hat{H}_1^0|F_1\rangle/\langle F_1|F_1\rangle$ is a minimum [17]. The rationale for this definition is that the minimum requirement, without the constraint that F_1 be a linear combination of the functions included in $\hat{Q}$, gives $F_1 = F_1^0$. One can show that this constraint implies that $\hat{Q}\hat{H}_1^0\hat{Q}F_1 = \varepsilon F_1$, and that this equation follows also from (5.2) [17]. Thus, if F_1 satisfies (5.2), it is *least distorted* from F_1^0 in the sense defined.

Equation (5.2) is nonlinear in F_1, but we have been able to solve it iteratively for H_2 and HeH^+ to rather high accuracy, using up to 500 two-electron configurations [18,19]. Similar calculations on LiH have not been done, and they may be impossible to do because of the unphysical states which are lower in energy than the physical ground state. Calculations like those in section 2 should be difficult to do with $\hat{\mathcal{H}}_H$, particularly in the neighborhood of the avoided crossings that must be present in the spectrum of $\hat{\mathcal{H}}_H(\lambda)$.

5.2. SIMPLE LEVEL SHIFTED EFFECTIVE HAMILTONIAN

The HS method outlined above can be looked at as a prescription for converting a given Hamiltonian into a Hamiltonian for determining a function F_1 which is least distorted from F_1^0. Here, we apply the prescription to $\hat{\mathcal{H}}_e = \hat{H}_1^0 + \hat{V}_1 + B(1-\hat{\mathcal{A}})$, the first effective Hamiltonian introduced in section 4. When we substitute $\hat{V}_1 + B(1-\hat{\mathcal{A}})$ for $\hat{V}_1$ in eq. (5.3), we get a new HS effective Hamiltonian:

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{H}_1^0 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q} + B(1-\hat{\mathcal{A}}) - B\hat{Q}(1-\hat{\mathcal{A}})\hat{Q} \\ &= \hat{\mathcal{H}}_H + B(1-\hat{\mathcal{A}}) - B\hat{Q}(1-\hat{\mathcal{A}})\hat{Q}, \end{aligned} \tag{5.5}$$

one which should have no unphysical solutions lower in energy than the lowest energy physical solution. However, what have we really accomplished by doing this?

From the definition of $\hat{Q}$ in eq. (5.1), it follows that $\hat{Q}$ and $\hat{\mathcal{A}}$ commute. Furthermore, since $\hat{Q}^2 = \hat{Q}$, the last two terms on the right in (5.5) combine to give $B(1-\hat{\mathcal{A}})(1-\hat{Q})$. Thus, the Hamiltonian $\hat{\mathcal{H}}$ in (5.5) reduces to $\hat{\mathcal{H}} = \hat{\mathcal{H}}_H + B(1-\hat{\mathcal{A}})(1-\hat{Q})$. The perturbation expansions are developed from $\hat{\mathcal{H}}F_1 = \varepsilon F_1$. Since $\hat{Q}F_1 = F_1$, one sees that $\hat{\mathcal{H}}F = \hat{\mathcal{H}}_H F$. This will be true no matter how we introduce the expansion parameter λ as long as there is a factor of $1-\hat{Q}$ multiplying the level shift operator. The new HS effective Hamiltonian must give, therefore, the same perturbation expansion as the old one. Nothing is accomplished by using the effective Hamiltonian defined in (5.5).

5.3. EFFECTIVE HAMILTONIAN WITH SHIFTED AND TRANSFORMED UNPHYSICAL STATES

In section 4, we introduced the Hamiltonian $\hat{\mathcal{H}}_e = \hat{H} - (1-\mathcal{A})\hat{v}$ which has the same physical eigenfunctions and eigenvalues as $\hat{H}$, but for which the unphysical eigenfunctions and eigenvalues were those of $\hat{t}+\hat{g}$. We try here to use this effective Hamiltonian as the basis for an improved HS method.

The first problem we encounter in applying the HS prescription arises because, as we have demonstrated in this paper, $\hat{Q}$ must depend on one physical eigenfunction, say Φ_1, and a finite number of unphysical eigenfunctions of $\hat{\mathcal{H}}_e$. We have shown that F_1 is a linear combination of these functions such that F_1 is least distorted from F_1^0, and we have assumed implicitly that this makes F_1 differ little from F_1^0. However, this assumption must be false when the unphysical functions we mix with Φ_1 are as highly delocalized as the eigenfunctions of $\hat{t}+\hat{g}$, the Hamiltonian for an electron gas, must be.

We can redefine $\hat{\mathcal{H}}_e$ so that its physical eigenfunctions remain those of $\hat{H}$, and so that only the energies of those unphysical eigenfunctions not appearing in $\hat{Q}$ are transformed and shifted to positive values. We set $\hat{\mathcal{H}}_e = \hat{H} - (1-\hat{Q})(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q})$. We substitute $\hat{V}_1 - (1-\hat{Q})(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q})$ for $\hat{V}_1$ in (5.1) to obtain

$$\hat{\mathcal{H}} = \hat{H}_1^0 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q} - (1-\hat{Q})(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q}).$$

If one assumes that $\hat{V}_1$ approaches zero as R approaches infinity, and that $\hat{Q}$ becomes $\hat{Q}^0$, then $\hat{\mathcal{H}}F_1^0 = \varepsilon^0 F_1^0$ in this limit, which is what we want. Unfortunately, this effective Hamiltonian has the same defect as the one proposed in the preceding subsection, namely, $\hat{\mathcal{H}}F_1 = \hat{\mathcal{H}}_H F_1$ because $(1-\hat{Q})F_1 = 0$. This means that the perturbation expansion that results with the above Hamiltonian must be identical to the HS expansion, which we believe to be divergent.

There is a way in which to fix what is wrong with the $\hat{\mathcal{H}}$ defined above, but it means not understanding the resultant effective Hamiltonian as well as we understand $\hat{\mathcal{H}}_H$. Consider the effective Hamiltonian

$$\hat{\mathcal{H}}_e = \hat{H} - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q}^0), \tag{5.6}$$

where $\hat{Q}^0$ is $\hat{Q}$ constructed from F_1^0. This Hamiltonian has the same physical eigenfunctions as $\hat{H}$ because $1-\hat{\mathcal{A}}$ commutes with $\hat{Q}^0$. Furthermore, in the limit $R=\infty$, all of the F_r^0 are eigenfunctions of this operator since $(1-\hat{Q}^0)F_r^0 = 0$. The unphysical eigenfunctions which are orthogonal to those which appear in $\hat{Q}^0$, must have positive energies since they are eigenfunctions of $(1-\hat{Q}^0)(1-\hat{\mathcal{A}})(\hat{t}+\hat{g})(1-\hat{Q}^0)$. From (5.6) and (5.1), substituting $\hat{V}_1 - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q}^0)$ for $\hat{V}_1$ in the latter, we arrive at a new HS effective Hamiltonian

$$\begin{aligned}\hat{\mathcal{H}} = {} & \hat{H}_1^0 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q} - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q}^0) \\ & + \hat{Q}(1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{v}(1-\hat{Q}^0)\hat{Q}.\end{aligned} \tag{5.7}$$

An HS-type perturbation method based on this $\hat{\mathcal{H}}$ will definitely not give the same expansion as $\hat{\mathcal{H}}_{\mathrm{H}}$ since $\hat{\mathcal{H}}F_1 \neq \hat{\mathcal{H}}_{\mathrm{H}}F_1$.

One preliminary test that must be passed if the perturbation expansion based on (5.7) is to converge for physical functions is that the eigenvalues of (5.6) as functions of the expansion parameter λ should have no avoided crossings involving the eigenvalues of physical functions. We can check this by ab initio calculations using the programs described in section 2. Two sets of calculations will be necessary because there are two ways in which we can introduce λ, namely,

$$\hat{\mathcal{H}}_{\mathrm{e}1}(\lambda) = \hat{H}_1^0 + \lambda[\hat{V}_1 - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{\upsilon}(1-\hat{Q}^0)], \tag{5.8a}$$

$$\hat{\mathcal{H}}_{\mathrm{e}2}(\lambda) = \hat{H}_1^0 - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{\upsilon}(1-\hat{Q}^0) + \lambda\hat{V}_1. \tag{5.8b}$$

The second effective Hamiltonian introduces an alternative to $\hat{H}_1^0$ as the unperturbed Hamiltonian, $\hat{\mathcal{H}}_1^0 = \hat{H}_1^0 - (1-\hat{Q}^0)(1-\hat{\mathcal{A}})\hat{\upsilon}(1-\hat{Q}^0)$. One can verify that F_1^0 is an eigenfunction of $\hat{H}_1^0$. We have not been able to do calculations with these Hamiltonians in time for this paper, but we believe that the lowest eigenvalue of $\hat{\mathcal{H}}_{\mathrm{e}1}(\lambda)$ will undergo no avoided crossings for $\lambda < 1$. We believe this is because the eigenvalues of $\hat{H}_1^0$ and $\hat{H}$ at infinite R are in one-to-one correspondence up to the energy of the ionic state $\mathrm{Li}^+\mathrm{H}^-$. At $\lambda = 1$ there is the potential for an avoided crossing because the effect of the projector $1-\hat{Q}^0$ at infinite R is to make the unphysical functions derived from F_1^0 degenerate with F_1^0 again. We expect a similar effect at finite R. The behavior to be expected of the $\hat{\mathcal{H}}_{\mathrm{e}2}(\lambda)$ eigenvalues is not obvious to us.

The HS perturbation equations based on taking $\hat{H}_1^0$ as the unperturbed Hamiltonian and the rest of $\hat{\mathcal{H}}$ in eq. (5.7) as the perturbing potential can be derived easily from the equations given in ref. [6]. We expand all quantities which depend on λ in power series, e.g. $\hat{Q}(\lambda) = \hat{Q}^0 + \lambda\hat{Q}^{(1)} + \ldots$. We find that $F_1^{(1)}$, the first-order function, is determined by

$$\left(\hat{H}_1^0 - \varepsilon^0\right)F_1^{(1)} = -(1-\hat{Q}^0)\hat{V}_1F_1^0, \tag{5.9}$$

the first-order correction to ε^0 being 0. This equation is identical to the equation for the first-order wave function in the HS method [6]. Since the second-order energy is determined by F_1^0 and $F_1^{(1)}$, the second-order energy we calculate with this new HS method will be exactly equal to what is obtained with the old. The operator $\hat{\upsilon}$ will appear first in the third-order energy, i.e., the new method is not identical to the old, it gives a different perturbation expansion. The new method is based on a Hamiltonian which, by design, is expected to have no unphysical-states problem and, consequently, may give a convergent expansion. Our tentative conclusion: the old HS method is correct through second order in the energy.

Assuming that $\hat{\mathcal{H}}_{\mathrm{e}2}$ does not have an unphysical-states problem, we can develop an alternative HS method based on $\hat{\mathcal{H}}_1^0$ as the unperturbed Hamiltonian, the perturbation being the rest of $\hat{\mathcal{H}}$ as defined in (5.7). The resultant perturbation equations through first order in λ are

$$\left(\hat{\mathcal{H}}_1^0 - \varepsilon^0\right)F_1^0 = \varepsilon^0 F_1^0, \tag{5.10a}$$

$$\left(\hat{\mathcal{H}}_1^0 - \varepsilon^0\right)F_1^{(1)} = -(1-\hat{Q}^0)\hat{V}_1 F_1^0 + \varepsilon^{(1)} F_1^0. \tag{5.10b}$$

The right-hand side of (5.10b) can be simplified by showing that $\varepsilon^{(1)}$ vanishes. These two equations differ from the old HS equations [6] by having $\hat{H}_1^0$ replaced by $\hat{\mathcal{H}}_1^0$. It follows that the expansion of $E(\lambda)$ will begin in second order to differ from the HS expansions that were previously derived [6]. It is also likely that the coefficients in the $1/R$ expansion calculated from the second-order energy will differ from those found in the polarization approximation, due to the difference between $\hat{\mathcal{H}}_1^0$ and $\hat{H}_1^0$. All of this is not consistent with the tentative conclusion of the preceding paragraph, but it remains to be seen that $\hat{\mathcal{H}}_{e2}(\lambda)$ has a spectrum consistent with a convergent perturbation expansion.

Our goal in this section was to save the HS method. Although further work is needed to see if we have succeeded, we believe that we have made some progress towards that goal.

6. Discussion

We began the work on which this paper is based with the belief that the better one understands the problem posed by unphysical states in the theory of interacting atoms and molecules, the more chance one has of solving it. The ab initio calculations discussed in sections 2 and 3 verify that unphysical states are a real problem and that perturbation expansions in λ must diverge, as had been expected [1,10]. The problem is formidable, obtaining convergence to one physical state when there are an infinite number of lower energy unphysical states with which the physical state can interact [2], but we know that it is not unsolvable because there are at least three effective Hamiltonians which potentially eliminate the problem for the physical ground state [3]. These effective Hamiltonians have the drawback that they do not give correctly in second-order the leading terms in the asymptotic $1/R$ expansion of the energy. Our goal has been to design a better effective Hamiltonian than any previously proposed.

One can ask, do we need anything better than the polarization approximation? It is a straightforward method, simply the Rayleigh–Schrödinger perturbation theory with the zeroth-order Hamiltonian $\hat{H}_1^0$ equal to the sum of the atomic Hamiltonians. And it does give correctly the leading $1/R$ coefficients in second order. If one is only interested in the asymptotic $1/R$ behavior of the energy, one needs nothing more. If, however, one calculates even the second-order energy at separations R where exchange energy begins to become significant, one has no idea how much in error that energy must be. All we are really sure of is that the second-order energy is part of a divergent series in the expansion parameter λ at finite R, but that as $R \to \infty$ it is asymptotically correct. That the series diverges has been clear since the work of Claverie. Any hope that for some unknown reason the series would converge should be dispelled by the calculations in section 2.

The three effective Hamiltonians, which have no unphysical-states problem in the limit of infinite R, differ from $\hat{H}(\lambda)$ in ways which raise all unphysical state energies above the energy of the physical ground state. Since we are interested only in the physical states, it should not matter how the unphysical states are transformed and shifted about. Thus, an obvious starting point for designing a better effective Hamiltonian is to look for operators which can sweep the unphysical states to higher energies. All of the effective Hamiltonians considered in this paper do this.

There is more to designing an effective Hamiltonian than taking care of the unphysical states. We found in section 4 that we could not develop from the effective Hamiltonian that we had defined there: perturbation expansions in λ that had properties consistent with what one should reasonably expect. What we expected was based on choosing $\hat{H}_1^0$ as the zero-order Hamiltonian at all nuclear separations. Thus, the zero-order wave function is the spin-projected product of atomic functions F_1^0 and the zero-order energy is ε^0, the sum of atomic energies. With these choices made, it is reasonable to want the first and all higher order corrections to vanish as $R \rightarrow \infty$ since the interatomic potential should vanish in that limit. Furthermore, one wants the correction to F_1^0 to be small, but this is not the case if the perturbation expansion must transform F_1^0 into the physical ground state function Φ_1. The correction can not be small because $\Phi_1 \propto \hat{\mathcal{A}} F_1^0$ at infinite R, so that the overlap integral between F_1^0 and Φ_1 is very small even for two Ne atoms. If the perturbation expansion transforms F_1^0 into Φ_1, one of its major effects must be to antisymmetrize F_1^0, a result which can be more efficiently achieved using $\hat{\mathcal{A}}$. We did not consider the alternative of using $\hat{\mathcal{A}} F_1^0$ as the unperturbed wave function because we did not find a suitable zero-order Hamiltonian.

The problems encountered in section 4 suggested that we try a more sophisticated method for arriving at an effective Hamiltonian, one better suited to the development of a perturbation expansion with acceptable properties. The HS concept, reworked [17], is effectively a prescription for writing down an effective Hamiltonian that has as one of its eigenfunctions a function F_1 which is *least distorted* from F_1^0 in an energy sense and which satisfies $\hat{\mathcal{A}} F_1 \propto \Phi_1$. In addition, it is known that the HS perturbation method gives the asymptotic $1/R$ depedence of the energy correctly in second order. The immediate result of applying the prescription to the two effective Hamiltonians from section 4 was two deadends, but the second suggested the adjustments which led to the effective Hamiltonians in eqs. (5.6) and (5.7). In short, our design effort did not give directly an acceptable effective Hamiltonian, but it led us to one.

What we have not yet done is to check the spectra of the effective Hamiltonians defined in eqs. (5.6)–(5.8) for avoided crossings as λ increases from 0 to 1. Until we have done these calculations, (5.8a) and (5.8b) should be regarded only as potential solutions to the unphysical-states problem. (Some calculations with level shifted Hamiltonians have been done since this paper was completed [20].)

What we have done in this paper must appear highly artificial and unphysical, and it largely is. On the other hand, we are trying to solve a mathematical problem which arises because we are imposing on a many-electron system an artificial, conceptual picture. What is conceptually interacting atoms or molecules is physically a collection of nuclei and indistinguishable electrons. As long as we maintain the indistinguishability of the electrons, there is no unphysical-states problem. It is when we divide the electrons into distinguishable groups that the unphysical solutions to the Schrödinger equation become a problem.

Acknowledgements

The calculations were made possible by a generous grant of time on the IBM 3081 at Rutgers University Computer Services.

Appendix

In section 2, we said that the $\hat{\mathcal{P}}_{ij}$ can not be represented in the bideterminantal basis used for LiH, but that $\hat{\mathcal{P}}_l$ could be. We also asserted that the application of $1 - \hat{\mathcal{P}}_l$ and of $3 + \hat{\mathcal{P}}_l$ to an eigenfunction of $\hat{H}^0$ gives an infinite separation, a physical and an unphysical eigenfunction of $\hat{H}$, respectively. Here, we sketch explanations for these statements.

Consider the product of a Slater determinant of the spin-orbitals ψ_1, ψ_2 and ψ_3 for electrons 1, 2 and 3, with single orbital $\varphi(4)$ for electron 4. We write $D(\psi_1, \psi_2, \psi_3)_{1,2,3}$ for this Slater determinant, the electron coordinates being indicated by the subscript. It follows that

$$\hat{\mathcal{P}}_l D(\psi_1, \psi_2, \psi_3)_{1,2,3}\, \varphi(4) = D(\psi_1, \psi_2, \psi_3)_{4,2,3}\, \varphi(1)$$

$$+ D(\psi_1, \psi_2, \psi_3)_{1,4,3}\, \varphi(2) + D(\psi_1, \psi_2, \psi_3)_{1,2,4}\, \varphi(3).$$

Expand each determinant on the right in minors along the row containing the ψ_k which depend on coordinate 4. Rearrange the terms in the resultant sum into three groups, so that one can factor out $\psi_1(4)$ from the first group, $\psi_2(4)$ from the second, and so on. The group of three terms multiplying $\psi_1(4)$ sums to the determinant $D(\varphi, \psi_2, \psi_3)_{1,2,3}$. Similarly, $\psi_2(4)$ and $\psi_3(4)$ are seen to be multiplied by determinants. Thus,

$$\hat{\mathcal{P}}_l D(\psi_1, \psi_2, \psi_3)_{1,2,3}\, \varphi(4) = D(\varphi, \psi_2, \psi_3)_{1,2,3}\, \psi_1(4)$$

$$+ D(\psi_1, \varphi, \psi_3)_{1,2,3}\, \psi_2(4) + D(\psi_1, \psi_2, \varphi)_{1,2,3}\, \psi_3(4).$$

This is a special case of a general result, $\hat{\mathcal{P}}_l$ applied to a bideterminantal function gives a sum of bideterminantal functions with the same partitioning of coordinates between the determinants as in the original function. The sum can be generated by summing over all single interchanges of orbitals between the original two determinants. For LiH, one can show by inspection that $\hat{\mathcal{P}}_{ij}$ applied to a bideterminantal function does not give a bideterminantal function, or a sum of bideterminants, with the same partitioning of electrons between the determinants as in the original function.

The easiest way we know to show that at infinite R one obtains eigenfunctions of $\hat{H}$ from those of $\hat{H}^0$ by applying $1-\hat{\mathcal{P}}_l$ and $3+\hat{\mathcal{P}}_l$ is to introduce a function $\chi_1 = \Phi(1, 2, 3)\varphi(4)$, where $\Phi(1, 2, 3)$ is totally antisymmetric in the coordinates 1, 2 and 3. This function has the same permutational symmetry as the eigenfunctions of $\hat{H}^0$. Define $\chi_{k+1} = \hat{\mathcal{P}}_{k,4}\chi_1$. Since the $\hat{\mathcal{P}}_{ij}$ operators commute with $\hat{H}$, one can easily show for $k = 2$ to 4 that $\langle \chi_k | \hat{H} | \chi_k \rangle = \langle \chi_1 | \hat{H} | \chi_1 \rangle = a$, the precise value of which is unimportant to our argument. Similarly, for $k = 2$ to 4, one must have $\langle \chi_1 | \hat{H} | \chi_k \rangle = \langle \chi_1 | \hat{H} | \chi_2 \rangle = b$. Finally, one can show that $\langle \chi_4 | \hat{H} | \chi_2 \rangle = \langle \chi_3 | \hat{H} | \chi_2 \rangle = \langle \chi_4 | \hat{H} | \chi_3 \rangle = -b$. The matrix of $\langle \chi_k | \hat{H} | \chi_l \rangle$ has a nondegenerate eigenvalue equal to $a - 3b$ and a threefold degenerate eigenvalue equal to $a + b$. The unnormalized eigenvector which gives the first eigenvalue is $[1, -1, -1, -1]$. The eigenvalue $a + b$ is obtained with the unnormalized eigenvectors $[3, 1, 1, 1]$, $[0, 2, -1, -1]$ and $[0, 0, 1, -1]$. Note that none of these eigenvectors depend upon a or b, they are determined by the permutational symmetry which was used in calculating the matrix elements. The same result can be obtained by using operators which project onto irreducible representations of the symmetric group.

The function corresponding to the vector $[1, -1, -1, -1]$ is $(1 - \hat{\mathcal{P}}_l)\chi_1$. That the resultant sum of the four χ_k's is antisymmetric, i.e., physical, is easy to verify by application of the $\hat{\mathcal{P}}_{ij}$. Also, if Φ is approximated by a 3-electron Slater determinant, $(1 - \hat{\mathcal{P}}_l)\chi_1$ can be represented in the bideterminantal basis. One can, in fact, show that this sum is a 4-electron Slater determinant. The vector $[3, 1, 1, 1]$ gives the function $3\chi_1 + \chi_2 + \chi_3 + c_4 = (3 + \hat{\mathcal{P}}_l)\chi_1$. Thus, if Φ is a 3-electron Slater determinant, $(3 + \hat{\mathcal{P}}_l)\chi_1$ can be represented in the bideterminantal basis. One can verify that this function can not be made antisymmetric, i.e., it is unphysical, by applying $(1 - \hat{\mathcal{P}}_l)$ to it. The result is zero. The remaining two vectors give functions which are not representable in the bideterminantal basis.

The symmetric group, irreducible representations of the physical and unphysical states of LiH can be found in the paper by Kutzelnigg [10].

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