PHYSICAL REVIEW A VOLUME 15, NUMBER 6 JUNE 1977

Many-body scattering theory methods as a means for solving bound-state problems: Applications of arrangement-channel quantum mechanics

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(Received 4 October 1976)

We propose in this article that the non-Hermitian equations typical of some many-body scattering theories be used to help solve many-body bound-state problems. The basic idea is to exploit the channel nature of many-body bound states that must exist because bound states are obvious negative-energy extensions of scattering states. Since atomic, molecular, and nuclear systems all display multichannel effects for $E > 0$, at least through Pauli-principle effects if not through mass-transfer reactions, this use of positive-energy methods for solving bound-state problems could have wide applicability. The development used here is based on the channel-component-state method of the channel-coupling-array theory, recently described in detail for the $E > 0$ case, and various aspects of the formalism are discussed. Detailed calculations using simple approximations are discussed for H_2^+, one of the simplest systems displaying channel structure. Comparison with the exact, Born-Oppenheimer results of Wind show that the non-Hermitian-equation, channel-component values of the equilibrium separation and total binding energy are accurate to within 2%, while the dissociation energy is accurate to 10%. The resulting wave function is identical to that arising from the simplest MO calculation, for which these numbers are less accurate than the preceding by at least a factor of 3. We also show that identical particle symmetry for the H_2^+ case reduces the pair of coupled (two-channel) equations to a single equation with an exchange term. Similar reductions will occur for larger numbers of identical particles, thus suggesting application of the formalism to atomic structure problems. A detailed analysis of the present numerical results, their general implications, and possible applications is also given.

I. INTRODUCTION

One of the most obvious physical differences between the positive energy ($E>0$) two-particle and n-particle problems is the existence, for $n>2$, of different arrangement channels. These channels correspond to the different ways in which the n particles can be partitioned into clusters of bound states, and subsequently observed. In the language of nuclear physics, they are the various reaction channels, although it is evident that such channels occur in atomic and molecular problems as well as in nuclear ones. Channels are easily described, as the following schematic example shows. Let A, B, C, etc., denote clusters of bound states containing at least 2 particles, and let a, b, c, etc. denote single particles (where we assume that the n particles of interest are distinguishable). A representative group of channels are

$a+A$, $b+B$, $W+Y$, 2-body channels;

$a+b+C$, $R+T+S$, 3-body channels;

$a+b+c+D$, 4-body channel;

$a+b+c+d+\cdots n$, n-body (break up) channel; etc.

These different channels are defined in different parts of configuration space, and correspond to states which are asymptotically orthogonal.

The existence of channels implies that the theory underlying the analyses of the $n=2$ and $n>2$ problems is also very different. For the $n=2$ case, either the Schrödinger equation plus the outgoing-wave-boundary condition or the Lippmann-Schwinger (LS) equation may in principle be used. However, when $n>2$, it is well known that a single LS equation alone is inadequate to uniquely specify the total scattering state, while on the other hand it is a nontrivial problem to introduce the various channels into the Schrödinger equation, i.e., through proper specification of the boundary conditions in all channels (especially m-body channels, $m\geq 3$). These latter problems have been eliminated by reformulations of the many-body ($n>2$) scattering problem. The most common procedure for effecting this is the use of coupled, integral equations for the transition operators whose on-shell matrix elements give the amplitudes for transitions between states in the various channels. These are collectively known as connected kernel equation (CKE) methods, since the equations are constructed to have kernels whose finite iterates are connected, i.e., do not suffer from divergences due to the presence of noninteracting particles.[1]

The effect of these CKE methods is to make

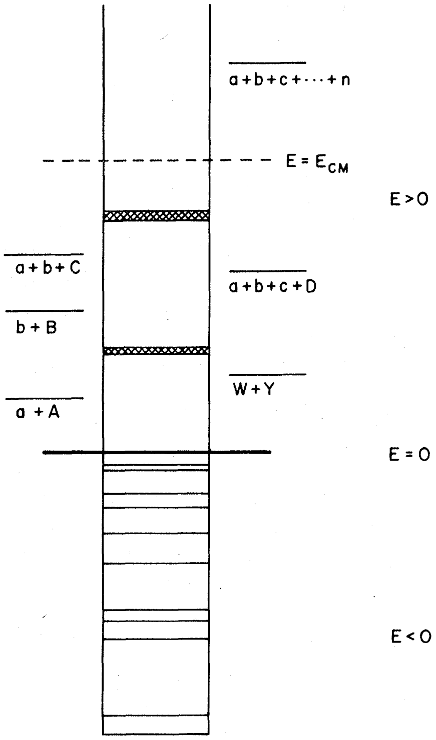

FIG. 1. Schematic spectrum of H, showing bound states (horizontal lines for $E<0$), resonances (cross-hatched regions), and thresholds for various m-body channels.

manifest the coupling and interaction of the various channels. That is, for sufficiently large $E>0$, asymptotic states can be found in different channels, and in order to understand the behavior of the n-particle system in one channel, we must in principle understand its behavior in every channel. This is easily seen in a schematic representation of the spectrum of H, as in Fig. 1. At the value of $E=E_{cm}$, which is well above the thresholds for various channels, it is apparent that the processes occurring in one channel influence those in another. This is seen in a more quantitative way on examination of the relation obeyed by the discontinuity of any transition operator: it is given by an on-shell sum of products of transition operators, with the sum occurring over all open channels.[2]

These comments about the $n>2$ problem emphasize well-known aspects of the $E>0$ part of the many-body spectrum. Since there are very obvious connections between the $E>0$ and $E<0$ portions of the spectrum, one may well expect to find direct effects of the channel nature of the $E>0$ part of the spectrum in the $E<0$ portion. This is, of course, not a new idea. In nuclear physics, one manifestation has long been known as clustering effects in nuclei,[3] while in molecular physics it occurs as, e.g., LCAO descriptions of molecular orbitals.[4] To our knowledge, however, there is no systematic, theoretically well-founded method for including such effects in the description of many-body bound states. Rather, *ad hoc* prescriptions only seem to be followed. Nevertheless, many-body scattering methods do exist which can be used as a basis for including $E>0$ channel effects in the $E<0$ case. Our purpose in this article is to examine one such class of methods and to emphasize the role that channels may play in bound-state problems. To some extent this paper is speculative in nature, since the stress is mainly on probable roles of channel effects. However, our speculations have been motivated by the results of calculations for a particular system, that of H_2^+; these are discussed in the final section of this paper.

The many-body formalism on which our discussion is based is that of the channel-coupling array theory[5] as expressed in the channel-component state form.[6,7] There are two reasons for this choice of method. First, the channel-coupling array theory is general. For $n=3$, there is a choice of the channel-coupling array W which leads to the Faddeev equations for the channel-component states, while for arbitrary n, an analogous choice of W leads to the Bencze-Redish transition operator equations.[8] In addition, there is also the channel permuting array (CPA) choice of W which leads to an alternate set of CKE's.[5] The second reason for using the W-array theory in channel-component form is that the channel components $|\psi_j\rangle$, when $E>0$, display the property that when j is a two-body channel, only $|\psi_j\rangle$ contributes to the scattering in that channel: $|\psi_m\rangle$, $m\neq j$, does not contribute.[9] This allows for simple interpretations of $|\psi_j\rangle$ and also provides suggestions as to how the $|\psi_j\rangle$ may be approximated when $E<0$.

In the remainder of this paper, we consider how the $E>0$ channel coupling method can be applied to the $E<0$ case. Section II deals, in two major subsections, with the theory. Subsection A reviews the $E>0$ case, discussed in detail in I, while in subsection B we examine various aspects of the $E<0$ situation. In the final section, several of the approximation methods of Sec. II B are applied to the simple but nontrivial example of the H_2^+ system. Effects of particle identity are discussed in detail for this example as well.

II. THEORY

A. $E>0$

As in previous work, we assume that the (distinguishable) n-particle Hamiltonian H can be partitioned into a channel Hamiltonian H_j and a channel interaction V_j in N ways:

$$H = H_j + V_j \ , \quad 1 \le j \le N \ . \tag{1}$$

Here H_j describes the internal states of the clusters forming channel j plus their relative motion, and V_j is the set of intercluster interactions. The number of channels N is assumed to include at least all two-body channels. We also write

$$H_j = K_j + h_j \ , \tag{2}$$

where K_j is the Hamiltonian for the relative motion, and h_j is the Hamiltonian for the internal states:

$$[\epsilon_j(\gamma) - h_j] \, | \varphi_j(\gamma) \rangle = 0 \ , \tag{3}$$

where γ is a complete set of quantum numbers for the state. We shall use the subscript b, i.e., γ_b, to indicate bound states and the label $j = 0$ for the n-body breakup channel, so that H_0 is the sum of all kinetic energy operators and V_0 is the sum of all interactions.

The Schrödinger equation is

$$(E - H) | \Psi \rangle = 0 \ , \tag{4}$$

subject to the usual boundary conditions for $E < 0$ and $E > 0$. In the channel-coupling-array theory which we follow here, *channel-component states* $|\psi_j\rangle$ are introduced via

$$|\Psi\rangle = \sum_j |\psi_j\rangle \ , \tag{5}$$

where $\sum_j$ is assumed to include at least all two-body channels. Then, in analogy to (4), the $|\psi_j\rangle$ are defined[6,7] to obey the set of coupled equations

$$\sum_m H_{jm} |\psi_m\rangle = E |\psi_j\rangle \ , \tag{6}$$

or in matrix form

$$\underline{H} |\underline{\psi}\rangle = E |\underline{\psi}\rangle \ , \tag{7}$$

with

$$\underline{H} = \underline{H}_0 + \underline{V} \ , \tag{8}$$

$$(\underline{H}_0)_{jk} = H_j \delta_{jk} \ , \tag{9}$$

and

$$(\underline{V})_{jk} = W_{jl} V_k \ . \tag{10}$$

The quantity W_{jl} in (10) is an element of the (real) channel-coupling array $\underline{W}$, an $N \times N$ matrix chosen for $E > 0$ to yield connected kernel integral equations.[5] The free channel index l may be chosen as is convenient, and it has been shown, e.g., in I, how to select l and W_{jl} so as to derive the Faddeev equations ($n = 3$, $N = 3$).[10] General discussions of $\underline{W}$ can be found in Refs. 5 and 7.

For $E > 0$, (7) is to be solved subject to the boundary conditions

$$|\underline{\psi}\rangle = |\underline{\phi}\rangle + \underline{G}_0(+) \underline{V} |\underline{\psi}\rangle \ , \tag{11}$$

where

$$[\underline{G}_0(+)]_{jk} = G_j(+) \delta_{jk} \equiv (E + i0 - H_j)^{-1} \delta_{jk} \tag{12}$$

and

$$(|\underline{\phi}\rangle)_j = |\Phi_k(E)\rangle \delta_{jk} \equiv |\vec{\mathrm{p}}_k\rangle \, |\varphi_k(\gamma_b)\rangle \delta_{jk} \ . \tag{13}$$

We assume that the initial channel k is a two-body channel; $|\vec{\mathrm{p}}_k\rangle$ is then a relative-motion plane wave state in channel k of momentum $\vec{\mathrm{p}}_k$. Solution of (11) leads to matrix elements of the transition operators $\hat{T}_{jk}(+)$ when j is a two-body channel and to matrix elements of the transition operators

$$U_{jk}^{(-)}(+) = \sum_m G_j^{-1}(+) G_m \hat{T}_{mk}(+)$$

when j is an m-body channel, $m > 2$, as discussed in Ref. 7. In each case, these matrix elements give the correct transition amplitudes.

A time-dependent analysis of scattering based on the channel scattering states was developed in Ref. 7. An apparent drawback to such a procedure, viz. the fact that $\underline{H}$ or approximations to it are not manifestly Hermitian (due to $\underline{V}^\dagger \ne \underline{V}$), was seen not to be a problem if H was invariant under rotations (at least about an axis of symmetry) and time reversal. For in this case, the vector $|\underline{\psi}\rangle$ could be defined to have a unique phase under action of the time reversal operator T, which is sufficient to guarantee that the energy E in Eq. (7) is real.[7] That is, imposition of the symmetries of H onto the solutions $|\underline{\psi}\rangle$ of $\underline{H}$ ensures that these solutions correspond to real energies. Alternatively, those $|\underline{\psi}\rangle$ which belong to complex energies do not have the requisite symmetry characteristics displayed by $|\Psi\rangle$, and thus, are inadmissable expansion states in (5).

For our needs in this work, we recall two important results of the time-dependent results.[7] First, it was shown that at time $t = 0$, the time-dependent vector of states $|\underline{\psi}(t = 0)\rangle$ was identical to the solution $|\underline{\psi}\rangle$ defined by Eq. (11). Second, and most important, it was shown that for m a two-body channel, only the state $|\psi_m\rangle$ in $|\Psi\rangle = \sum_j |\psi_j\rangle$ contributed to the scattering in channel m. That is,

$$\langle \vec{\mathrm{r}}_m, \varphi_m(\gamma_b') | \psi_j \rangle \underset{r_m \to \infty}{\sim} 0 \ , \quad j \ne m = 2\text{-body channel} \ .$$

Hence,

$$\begin{aligned} \langle \vec{\mathrm{r}}_m, \varphi_m(\gamma_b') | \Psi \rangle &= \langle \vec{\mathrm{r}}_m, \varphi_m(\gamma_b') | \sum_j \psi_j \rangle \\ &\underset{r_m \to \infty}{\sim} \langle \vec{\mathrm{r}}_m, \varphi_m(\gamma_b') | \psi_m \rangle \\ &\underset{r_m \to \infty}{\sim} \Big[e^{i \vec{\mathrm{p}}_k \cdot \vec{\mathrm{r}}_k} \delta_{\gamma_b' \gamma_b} \delta_{mk} \\ &\qquad + f_{m\gamma_b', k\gamma_b}(\vec{\mathrm{p}}_m, \vec{\mathrm{p}}_k) \frac{e^{i p_m r_m}}{r_m} \Big] \ , \end{aligned} \tag{14}$$

where f is the exact two-body scattering amplitude:

$$f_{m\gamma'_b,\,k\gamma_b}(\vec{\mathrm{p}}_m,\vec{\mathrm{p}}_k)\propto\langle\vec{\mathrm{p}}_m,\varphi_m(\gamma'_b)\,|\,\hat{T}_{mk}(+)\,|\,\varphi_k(\gamma_b),\vec{\mathrm{p}}_k\rangle\ . \tag{15}$$

The meaning of this result is that $|\psi_m\rangle$ is the portion of $|\Psi\rangle$ in channel m, i.e., $|\Psi\rangle$ is asymptotically equal to $|\psi_m\rangle$ in channel m, m being an arbitrary two-body channel. Thus, Eq. (5) is a valid "expansion" of $|\Psi\rangle$ into its various arrangement channel components.

As noted above, when m is a many-body channel ($m>2$), then (5) yields the matrix element of $U^{(-)}_{mk}(+)=\sum_j G_m^{-1}(+)G_j\hat{T}_{jk}(+)$ as the (correct) transition amplitude. Since $\sum_j|\psi_j\rangle$ must include all (open) two-body channels in order to obtain (14), but need not include *any* many-body channels by the preceding result, we draw the important conclusion that (5) is a valid expansion for $|\Psi\rangle$ as long as $\sum_j$ includes all but no more than the set of two-body channels. This is precisely the same conclusion resulting from the analysis of Benoist-Gueutal,[11] whose work implies that the minimum number of channels required in the coupled equations for the $\hat{T}_{jk}$ in order that the proper discontinuity relation be satisfied is the set of two-body channels. We shall thus assume that in (5), $\sum_j$ includes the set of two-body channels, and further, we shall carry over this assumption to the bound-state case ($E<0$).

B. $E<0$

The $E>0$ solutions of (7), subject to the boundary conditions implied by (11), lead to the correct scattering amplitudes, given as on-shell matrix elements of either $\hat{T}_{jk}(+)$ when j is a two-body channel or else of the operator $U^{(-)}_{jk}(+)$. Correspondingly, the poles of $\hat{T}_{jk}$ (or $U^{(-)}_{jk}$) will give the n-particle bound states. These could be obtained by solving the coupled equations for the $\hat{T}_{jk}$, but it is clearly easier to deal with the original equation for the $|\psi\rangle$, viz. Eq. (7), from which the coupled T-operator equations can be derived. The $E<0$ solutions of (7) will yield the bound states $|\Psi\rangle$ [through Eq. (5)] and the bound-state energies E of (4). In either case, that is, by finding the poles of the $\hat{T}_{jk}$ or the $E<0$ eigenvalues of (7), we incorporate into the description of many-body bound states the arrangement channel nature of the $E>0$ portion of the many-body spectrum as discussed in the Introduction. This may well prove to have useful consequences, as implied by the results of the H_2^+ calculation discussed in Sec. III. A comparison of shell-model calculations and those based on Eq. (7) is given below. Before discussing this topic we examine a number of aspects of the bound-state formalism provided by Eqs. (6) or (7) including the non-Hermiticity, the character or exact solutions, the meaning of the $|\psi_j\rangle$, various approximation methods, and the effect of choosing different kinds of W.

1. Non-Hermiticity of Equation (7)

Although the physical arguments presented in the Introduction indicate that the inclusion of channel effects into many-body bound-state problems is not unreasonable, the use of non-Hermitian equations to calculate such effects may seem surprising if not actually incorrect. In fact such equations arise in a straightforward way and are one of the differences between the $n=2$ and $n>2$ cases. Their existence is a direct manifestation of the non-Hermiticity of H when $E>0$, i.e., when (4) is no longer an eigenvalue problem.

Let us consider the $n=2$ case first. The non-Hermiticity of H is trivial to demonstrate. We shall use an arrow under the operator to indicate the direction in which it acts. Writing $H=H_0+V$, where H_0 is the kinetic energy and V is a local, real c-number potential, we have

$$H|\Psi\rangle=E|\Psi\rangle \quad\text{and}\quad H_0|\vec{\mathrm{k}}\rangle=E|\vec{\mathrm{k}}\rangle\ .$$

Then

$$\langle\vec{\mathrm{k}}|E-\underset{\rightarrow}{H}|\Psi\rangle=0$$

while

$$\langle\vec{\mathrm{k}}|E-\underset{\leftarrow}{H}|\Psi\rangle=\langle\vec{\mathrm{k}}|\underset{\leftrightarrow}{V}|\Psi\rangle\neq 0\ ,$$

thus establishing the non-Hermiticity of H for $E>0$. That is, in order for H to be a Hermitian operator, we must have

$$\langle\eta|\underset{\leftarrow}{H}|\zeta\rangle=\langle\underset{\rightarrow}{H}\eta|\zeta\rangle=\langle\eta|\underset{\rightarrow}{H}|\zeta\rangle$$

for *any* pair of states $|\eta\rangle$ and $|\zeta\rangle$.

Still continuing with the case $n=2$, we now ask for solutions to $H|\Psi\rangle=E|\Psi\rangle$ subject to the boundary condition implied by

$$|\Psi\rangle=|\vec{\mathrm{p}}\rangle+(E+i0-H_0)^{-1}V|\Psi\rangle\ .$$

This is the only boundary condition required because of the single-channel nature of the problem, and as is well known yields a unique solution of the Schrödinger equation. The differential form of this integral equation is of course just $H|\Psi\rangle=E|\Psi\rangle$.

Now consider the many-channel case, $n>2$. When $E>0$, the preceding proof of the non-Hermiticity of H is valid, except that it can occur in many more ways, since unperturbed states analogous to $|\vec{\mathrm{k}}\rangle$ of the $n=2$ case will occur in every channel. On the other hand, to solve the Schrödinger equation, it is insufficient to impose the boundary conditions by means of one integral equation alone, as proved in detail by Glöckle for the $n=3$ case,[12] since this does not lead to a unique solution. As remarked on in I, there are at least two distinct (families of) ways of specifying the boundary conditions. These are through the channel scattering states $|X_m\rangle$ and through the channel-component states $|\psi_j\rangle$. The differential form of the boundary-condition equations obeyed by both the $|X_m\rangle$ and the $|\psi_j\rangle$ are non-Hermitian matrix equations. This non-Hermiticity arises from the facts that H is non-Hermitian when $E>0$ and that an n-particle problem is also a multichannel problem. It is amusing to note that the differential equations for the channel scattering states all collapse to the Schrödinger equation once it is recalled[6] that each $|X_m\rangle$ is equal to $|\Psi\rangle$. However, the non-Hermitian form for the $|\psi_j\rangle$ is of persistent character. When different approximations for each channel are introduced however, both sets of equations remain in non-Hermitian form. As we show next, the exact solutions $|\psi_j\rangle$ to Eq. (6) provide the real eigenvalues and eigenstates of the Schrödinger equation.

2. *Exact solutions of (7)*

When $n=N=3$, it is possible to choose $\underline{W}$ so that (6) become the Faddeev equations for the wave-function components as shown in I. In that case, as proved by Faddeev,[10] the $E<0$ solutions of (6) are precisely the solutions of the Schrödinger equation (4). This proves that $\text{Im}\, E=0$, even though $\underline{H}^\dagger \neq \underline{H}$, as remarked on elsewhere.[13] For arbitrary n and N, Eq. (5) is the generalization of the Faddeev wave-function decomposition (see I for further discussion of this point). Although (6) [or (7)] is obtained from the Schrödinger equation whose bound-state energies are real, it is a non-Hermitian matrix equation and may admit of complex eigenvalues. We now show, independent of any assumptions about rotational or time-reversal invariance, that just as in the case of the Faddeev equations, exact solutions of (6) yield the (real) eigenvalues and the corresponding eigenstates of (4). This proof is based on that given in Ref. 6 and is similar to Faddeev's for the $n=3$ case.[10]

Let E in (6) be replaced by a possibly complex energy parameter z. On using Eqs. (8)–(10), (6) becomes

$$H_j|\psi_j\rangle + \sum_m W_{jl} V_m |\psi_m\rangle = z|\psi_j\rangle \; . \tag{16}$$

Summing both sides of (16) on j yields

$$\sum_j H_j|\psi_j\rangle + \sum_m V_m|\psi_m\rangle = z\sum_j |\psi_j\rangle \; , \tag{17}$$

where we have used $\sum_j W_{jl}=1$. Since m is a dummy index, (17) is easily seen to be equal to

$$\sum_j (H_j+V_j)|\psi_j\rangle = z\sum_j |\psi_j\rangle \; ,$$

or

$$H\sum_j |\psi_j\rangle = z\sum_j |\psi_j\rangle \; . \tag{18}$$

Because H is Hermitian for bound-state boundary conditions, (18) clearly implies that $\text{Im}\, z=0$ and $\sum_j |\psi_j\rangle = |\Psi\rangle$, which establishes the proof. Note that it is essential that in the sum on j, Eq. (17), the full Hamiltonian H is recovered from the sums $\sum H_j|\psi_j\rangle$ and $\sum V_m|\psi_m\rangle$ for each channel.

3. *Meaning of the $|\psi_j\rangle$ when $E<0$*

When $E>0$, $|\psi_m\rangle$ is the portion of $|\Psi\rangle$ in channel m. For example, let m be a two-body channel. Then we have

$$|\psi_m\rangle = \sum_b |\varphi_m(\gamma_b)\rangle |F_m(\gamma_b)\rangle + \int d\gamma\, |\varphi_m(\gamma)\rangle |F_m(\gamma)\rangle \; , \tag{19}$$

where $\int d\gamma$ means an integration over breakup state quantum numbers γ. The $|\varphi_m(\gamma_b)\rangle$ are the bound-state parts of the asymptotic states, and the usual outgoing wave boundary condition means that $\langle \vec{r}_m | F_m(\gamma_b)\rangle$ obeys the boundary condition of (14). Since $E<0$ is the negative-energy continuation of the $E>0$ case, it follows that for $E<0$, since there is no plane-wave term in $|F_m(\gamma_b)\rangle$, we have ($p_m \to i\alpha$):

$$\langle \vec{r}_m | F_m(\gamma_b)\rangle \;\propto\; e^{-\alpha r_m}/r_m \; , \quad r_m \to \infty \tag{20}$$

where α is a number characteristic of the state γ_b and the bound-state energy E. Similar comments hold for the states γ, and for general m-body channels.

The implication is that for $E<0$, $|\psi_m\rangle$ is still the "portion" of $|\Psi\rangle$ in channel m, in the sense that for large r_m, $\langle \vec{r}_m \varphi_m(\gamma_b)|\Psi\rangle = \langle \vec{r}_m, \varphi_m(\gamma_b)|\psi_m\rangle \propto e^{-\alpha r_m}/r_m$, $r_m \to \infty$. Hence, when $E<0$, $|\psi_m\rangle$ can still be meaningfully expanded in the set of states $\{\varphi_m(\gamma')\}$, exactly as in (19), although now bound-state boundary conditions apply. The expansion (19) will always hold when exact solutions are being considered, and suggests possible approximation procedures as well, which we consider next.

4. *Approximations*

For practical calculations it will be necessary to approximate in some way the solutions of Eq. (6).

This means that the resulting $\sum_j |\psi_j\rangle$ and E will be an approximation to $|\Psi\rangle$ and its Schrödinger equation eigenvalue. Hence, the first task is to ensure that the E obtained from the approximate calculation is real. We may distinguish two types of approximations: those that permit the summations similar to (17) to be done leading to an equation similar[14] to (18) and those that do not. In the former case we are ensured that $\operatorname{Im} z = 0$. In the latter case we have no such assurance, as already discussed in detail for the $n=3, N=3$ problem using the Faddeev equations,[13] and we therefore must rely on the (assumed) invariance properties of H and the behavior of $|\underline{\psi}\rangle$ under the time reversal operator T to guarantee the reality[7] of the negative energy eigenvalues of (6) under such approximations. For example, we assume an n-body system invariant under arbitrary rotations and T, and choose $|\underline{\psi}\rangle$ so that

$$\mathsf{T}\,|\underline{\psi}(JM)\rangle = \eta_{JM}\,|\underline{\psi}(J-M)\rangle, \tag{21}$$

where JM are the total angular momentum and its projection. Then (21) guarantees[7] that E of (6) is real. On the other hand for $|\underline{\psi}\rangle$ which does not have a fixed phase under T, no statements about reality can be made for approximations of the second kind, and we must expect E to be complex. Such values are to be rejected on the ground that invariance of H implies (21), so that $|\underline{\psi}\rangle$ which do not conform to (21) are unphysical. This is analogous to rejection of those $|\Psi\rangle$ which are symmetric under particle interchange for systems of identical fermions. We consider several different types of approximation schemes below.

a. Projection (diagonalization) techniques. This method has been briefly discussed in Ref. 13 for the three-body case, and we enlarge on that discussion here. The method appears to be one that could be used for a wide variety of physical systems. It is analogous to both coupled-channel approximation techniques for collisions and shell-model schemes for bound-state approximations to the Schrödinger Hamiltonian H.

We form projection operators P_j in each channel j as follows:

$$P_j = \sum_b |\varphi_j(\gamma_b)\rangle\rangle\langle\varphi_j(\gamma_b)|, \tag{22}$$

where $\sum_b$ includes at least one bound state. The approximation of interest here is then

$$\begin{aligned} |\psi_j\rangle \to |\tilde{\psi}_j\rangle &= P_j|\psi_j\rangle \\ &\equiv \sum_b |\varphi_j(\gamma_b)\rangle\rangle\,|F_j(\gamma_b)\rangle. \end{aligned} \tag{23}$$

That is, in each channel, at most the totality of bound states occurring in Eq. (19) is retained as the approximation. A further and to be expected approximation is that the $|\varphi_j(\gamma_b)\rangle\rangle$ themselves will be represented by model states, e.g., shell model, Hartree-Fock, molecular orbital, etc. Note that the j in (22) could refer to m-body channels, in which case the $|\varphi_j(\gamma_b)\rangle\rangle$ would be a product of m rather than two bound states. The $|F_j(\gamma_b)\rangle$ in all cases will obey Eq. (20), although for an m-body channel, $\vec{r}_j$ is to be taken as the relative coordinate of any one of the pairs of the m bound clusters.

Because $P_j^2 = P_j$ (although $[P_j, P_k] \neq 0$), we may rewrite (7) in this approximation as

$$\underline{\tilde{\mathrm{H}}}\,|\underline{\tilde{\psi}}\rangle = E\,|\underline{\tilde{\psi}}\rangle, \tag{24}$$

where

$$(\underline{\tilde{\mathrm{H}}})_{jk} = (\underline{\tilde{\mathrm{H}}}_0)_{jk} + (\underline{\tilde{\mathrm{V}}})_{jk},$$

with

$$(\underline{\tilde{\mathrm{H}}}_0)_{jk} = P_j H_j \delta_{jk} = H_j P_j \delta_{jk}$$

and

$$(\underline{\tilde{\mathrm{V}}})_{jk} = P_j W_{jl} V_k P_k.$$

In order to see how to use (24) to solve bound-state problems, we first consider the $E>0$ case and choose $\underline{\mathrm{W}}$ to be a channel permuting array $(l=k)$. Then (24) becomes

$$(E - H_j)\,|\tilde{\psi}_j\rangle = \sum_k W_{jk} P_j V_k P_k |\tilde{\psi}_k\rangle. \tag{25}$$

Although we are now working in a truncated Hilbert space, (25) must still lead to approximate scattering amplitudes determined from equations like (11) or (14). By construction [Eqs. (23)], these approximate amplitudes are obtained directly from $|F_j(\gamma_b)\rangle$. To get $|F_j(\gamma_b)\rangle$, we must project $|\tilde{\psi}_j\rangle$ onto $\langle\phi_j(\gamma_b)|$, *not* onto $\langle\phi_l(\gamma_{b'})|$, $l \neq j$. That is, $|\psi_j\rangle$ and the theory on which it is based[7] uniquely give the scattering amplitude only when projected onto a bound state in channel j. One could of course, project $|\psi_j\rangle$ onto $\langle\phi_l(\gamma_{b'})|$, but from the nature of the $|\psi_j\rangle$, as discussed in Ref. 7, this does not lead to the relevant scattering amplitude. In order to find it from such a projection, we would have to form

$$\sum\!\!\!\!\!\!\int |\phi_l(\gamma)\rangle\rangle\langle\phi_l(\gamma)|\psi_j\rangle$$

to get the exact amplitude; just how to get the corresponding approximate amplitude from $|\tilde{\psi}_j\rangle$ with an inappropriate projection is not clear, although we expect that $\sum|\phi_l(\gamma_b)\rangle\rangle\langle\phi_l(\gamma_b)|\tilde{\psi}_j\rangle$ will always be inadequate because even though $|\tilde{\psi}_j\rangle$ will be an approximation to $|\psi_j\rangle$, an *exact* representation of the approximate state requires an expansion in the continuum as well as the bound states from another channel.

Given this discussion, the correct procedure to follow for determining the $|F_j(\gamma_b)\rangle$ is to project (25) onto $\langle\phi_j(\gamma_b)|$, giving

$$[E-\epsilon_j(\gamma_b)-K_j]\,|F_j(\gamma_b)\rangle = \sum_k \sum_{b'} W_{jk}\langle\varphi_j(\gamma_b)|\,V_k\,|\varphi_k(\gamma_{b'})\rangle|F_k(\gamma_{b'})\rangle. \quad (26)$$

The approximate $k\rightarrow j$ scattering amplitude is uniquely obtained from this set of equations plus the boundary condition (11) as expressed in the form (14).

The fact that we are using the $E<0$ continuation of arrangement channel quantum mechanics to solve bound-state problems, means that (26) is the correct $E<0$ version of the theory to use in the approximate projection operator form. We stress this, since if one merely uses a projection approximation to (7) for $E<0$ without noting the $E>0$ and $E<0$ connection, projected equations other than (26) could be obtained as implied above. These, however, are to be rejected on the ground that they are not the correct $E<0$ continuation of the many-body scattering theory.

We also note that this approximation, i.e., (26), can be a diagonalization procedure, quite similar to that used in shell-model calculations. It appears in a natural manner for molecular physics calculations in the Born-Oppenheimer approximation ($K_j\cong 0$); this is illustrated for the H_2^+ system in the Sec. III, where the $|F_j(\gamma_b)\rangle$ are seen to be just normalization constants.

b. Perturbation theory. Since the equation obeyed by $|\underline{\psi}\rangle$ is identical in structure to the Schrödinger equation, the usual formulas of time-independent perturbation theory can *in principle* be carried over to the present case with no change other than the use of matrix notation. However, in addition to the usual cautions in applying perturbation theory indiscriminately,[15] there is an important difference between its use in (4) and in (7). One always assumes that in (4), H may be decomposed into an unperturbed part H_0 and a perturbation written as λV ($\lambda=1$ ultimately) such that H_0 supports bound states. In the form of perturbation theory we shall consider for (7), we first write $\underline{\mathrm{H}}=\underline{\mathrm{H}}_0+\lambda\underline{\mathrm{V}}$, treating $\lambda\underline{\mathrm{V}}$ as the perturbation with its "small" expansion parameter λ whose final value is unity.[16] For most cases, the structure of $(\underline{\mathrm{H}}_0)_{jk}=H_j\delta_{jk}$ implies that along the "direction" $\vec{r}_j$, we have a plane wave rather than a bound state. (For the Born-Oppenheimer type of approximation, as we shall see, this comment is not true, and the following construction need not be applied.) To ensure complete bound-state behavior for the solutions of $\underline{\mathrm{H}}_0$, we shall add and subtract attractive one-body potentials depending on $\vec{r}_j$, just as one adds and subtracts one-body optical potentials in the case of reactions.[17] Thus, we shall consider the modified problem

$$\underline{\mathrm{H}}=\underline{\mathrm{H}}_0^M+\underline{\mathrm{V}}^M, \quad (27)$$

with

$$\underline{\mathrm{H}}_0^M=\underline{\mathrm{H}}_0+\underline{\mathrm{U}} \quad (28)$$

and

$$\underline{\mathrm{V}}^M=\underline{\mathrm{V}}-\underline{\mathrm{U}}, \quad (29)$$

where

$$(\underline{\mathrm{U}})_{jk}=U_j\delta_{jk}$$

and U_j is the attractive potential producing at least one complete bound state in each channel. Examples of U_j could be an oscillator potential, a Woods-Saxon potential or a Morse potential. We shall assume that a U_j can be chosen to give accurate results, although this may well be a nontrivial problem.

The unperturbed states $|\underline{\chi}_\alpha\rangle$ obey

$$\underline{\mathrm{H}}_0^M|\underline{\chi}_\alpha\rangle=W_\alpha|\underline{\chi}_\alpha\rangle,$$

with a typical element of $|\underline{\chi}_\alpha\rangle$ being

$$(|\underline{\chi}_\alpha\rangle)_j=N^{-1/2}|\chi_j^{(\alpha)}(\gamma_b)\rangle, \quad (30)$$

where $|\chi_j^{(\alpha)}(\gamma_b)\rangle$ vanishes asymptotically and is assumed to be *normalized*: $\langle\chi_j^{(\alpha)}(\gamma_b)|\chi_j^{(\alpha)}(\gamma_b')\rangle=\delta_{\gamma_b\gamma'_b}$. Also, N is the dimension of the column vector $|\underline{\chi}_\alpha\rangle$. We now write $\underline{\mathrm{V}}^M\rightarrow\lambda\underline{\mathrm{V}}^M$ and seek the usual perturbative solutions of $\underline{\mathrm{H}}=\underline{\mathrm{H}}_0^M+\lambda\underline{\mathrm{V}}^M$. The usual formulas[15] now apply, where we note that matrix elements such as $\langle\underline{\chi}_\alpha|\underline{\mathrm{V}}^M|\underline{\chi}_\beta\rangle$ carry an implied transpose of the column vector $|\underline{\chi}_\alpha\rangle$ to the row vector $\langle\underline{\chi}_\beta|$.

If we assume that $|\underline{\chi}_\alpha\rangle$ is the solution when $\lambda=0$, then straightforward calculations give for the low-order terms in

$$|\underline{\psi}\rangle=\sum\lambda^n|\underline{\psi}^{(n)}\rangle$$

and

$$E=\sum\lambda^n E^{(n)},$$

the results

$$|\underline{\psi}^{(0)}\rangle=|\underline{\chi}_\alpha\rangle,\ E^{(0)}=W_\alpha \quad (31)$$

and

$$|\underline{\psi}^{(1)}\rangle=\sum_{\beta\neq\alpha}|\underline{\chi}_\beta\rangle\frac{\langle\underline{\chi}_\beta|\underline{\mathrm{V}}^M|\underline{\chi}_\alpha\rangle}{W_\alpha-W_\beta},\quad E^{(1)}=\langle\underline{\chi}_\alpha|\underline{\mathrm{V}}^M|\underline{\chi}_\alpha\rangle. \quad (32)$$

Higher-order terms follow from the standard single channel formulas.[15]

c. Variational principles. As in the preceding, we distinguish the various (exact) solutions to (7) by the collective label $\alpha(|\Psi\rangle \to |\Psi_\alpha\rangle)$:

$$\underline{\mathrm{H}}\,|\underline{\psi}_\alpha\rangle = E_\alpha\,|\underline{\psi}_\alpha\rangle, \tag{33}$$

where, e.g.,

$$(|\underline{\psi}_\alpha\rangle)_j = |\psi_j^{(\alpha)}(\gamma_b)\rangle \tag{34}$$

and we again consider only totally bound states. In addition, we choose the $|\psi_j^{(\alpha)}(\gamma_b)\rangle$ to be normalized:

$$\langle\psi_j^{(\alpha)}(\gamma_b)\,|\,\psi_j^{(\alpha)}(\gamma_b')\rangle = \delta_{\gamma_b\gamma_b'}. \tag{35}$$

Then, if there are N channels forming $\underline{\mathrm{H}}$, (33) is clearly equivalent to

$$E_\alpha = N^{-1}\langle\underline{\psi}_\alpha|\underline{\mathrm{H}}|\underline{\psi}_\alpha\rangle. \tag{36}$$

Goldflam and Kouri[18] have noted that because $\underline{\mathrm{H}}^\dagger \neq \underline{\mathrm{H}}$, (36) does not provide a starting point for obtaining a variational bound to E_α. Their solution of the problem was to define a normalization matrix $\underline{\mathrm{N}}$ such that $\langle\underline{\psi}_\alpha|\underline{\mathrm{N}}|\underline{\psi}_\alpha\rangle = 1$, and use $\underline{\mathrm{N}}$ to obtain the standard Rayleigh-Ritz bound. We proceed differently, as follows.

The problem with using (36) as a starting point is that $\langle\underline{\psi}_\alpha|$ is not known to be an eigenstate of $\underline{\mathrm{H}}$ when it acts to the left. However, the *channel scattering states* $|X_m\rangle$ discussed in detail in I, *do* satisfy

$$\langle\underline{\mathrm{X}}|\underline{\mathrm{H}} = E\langle\underline{\mathrm{X}}|, \tag{37a}$$

or equivalently

$$\underline{\mathrm{H}}^T|\underline{\mathrm{X}}\rangle = E|\underline{\mathrm{X}}\rangle, \tag{37b}$$

and as such can be used in a variational principle in the standard manner.[19] We have here introduced the row and column vectors $\langle\underline{\mathrm{X}}|$ and $|\underline{\mathrm{X}}\rangle$ with elements $\langle X_m|$ and $|X_m\rangle$. The proof that $|\underline{\mathrm{X}}\rangle$ obeys (37b) follows from the integral equation for the $|X_m\rangle$ discussed in I, which is of the form

$$|\underline{\mathrm{X}}\rangle = |\underline{\phi}\rangle + \underline{\mathrm{G}}_0(+)\underline{\mathrm{V}}^T|\underline{\mathrm{X}}\rangle;$$

the presence of $\underline{\mathrm{V}}^T$ implies (37b).

The starting point of our variational approach will thus be

$$E_\alpha = \frac{\langle\underline{\mathrm{X}}_\alpha|\underline{\mathrm{H}}|\underline{\psi}_\alpha\rangle}{\langle\underline{\mathrm{X}}_\alpha|\underline{\psi}_\alpha\rangle}, \tag{38}$$

rather than Eq. (36). However, since $|\underline{\mathrm{X}}\rangle$ obeys (37b) while $|\underline{\psi}\rangle$ obeys (7), the relationship between them must be established, in particular, the meaning of the collective index α on $|\underline{\mathrm{X}}_\alpha\rangle$. The key point here is the fact that for exact solutions to (37b), we know[7] that

$$|X_m^{(\alpha)}\rangle \equiv |\Psi_\alpha\rangle, \quad \text{all } m, \tag{39}$$

and equivalently, $\langle X_m^{(\alpha)}| = \langle\Psi_\alpha|$. Therefore it follows from (5) and (39) that

$$\langle X_m^{(\alpha)}| = \sum_j \langle\psi_j^{(\alpha)}|, \quad \text{all } m. \tag{40}$$

Furthermore, these latter results imply that $|\underline{\mathrm{X}}_\alpha\rangle$ has the same property under time reversal as do the $|\underline{\psi}_\alpha\rangle$ and $|\Psi_\alpha\rangle$. Thus the proof used in I to establish reality of E is valid for Eq. (38) also.

Statement of the variational principle is now straightforward. We define the functional $I[|\underline{\mathrm{f}}\rangle]$ by

$$I[|\underline{\mathrm{f}}\rangle] = \frac{\langle\underline{\mathrm{F}}|\underline{\mathrm{H}}|\underline{\mathrm{f}}\rangle}{\langle\underline{\mathrm{F}}|\underline{\mathrm{f}}\rangle}, \tag{41}$$

where

$$(\langle\underline{\mathrm{F}}|)_m = \sum_j \langle f_j|, \quad \text{all } m. \tag{42}$$

When $|\underline{\mathrm{f}}\rangle = |\underline{\psi}_\alpha\rangle$, we have $I[|\underline{\psi}_\alpha\rangle] = E_\alpha$. When $|\underline{\mathrm{f}}\rangle = |\underline{\psi}_\alpha\rangle + \delta|\underline{\psi}_\alpha\rangle$, we find using $\langle\underline{\mathrm{X}}|(E_\alpha - \underline{\mathrm{H}}) = 0$ that $\delta I[|\underline{\psi}_\alpha\rangle] = 0$, and hence $I[|\underline{\mathrm{f}}\rangle]$ is stationary about the exact solution $|\underline{\psi}_\alpha\rangle$. Finally, if we expand $|\underline{\mathrm{f}}\rangle$ in the complete set of states $|\underline{\psi}_\alpha\rangle$,

$$|\underline{\mathrm{f}}\rangle = \sum_\alpha c_\alpha|\underline{\psi}_\alpha\rangle, \tag{43}$$

we obtain

$$I[|\underline{\mathrm{f}}\rangle] \geq E_0, \tag{44}$$

where $\alpha = 0$ denotes the ground state. That is, $I[|\underline{\mathrm{f}}\rangle]$ provides an upper bound to the ground-state energy of the n-particle system. In particular, if $|\underline{\mathrm{f}}\rangle$ is replaced by a vector of trial functions $|\underline{\psi}_t\rangle$ containing $M \times N$ variational parameters $a_j^{(i)}$, then an upper bound to E_0 is obtained by solving for the parameters $a_j^{(i)}$ through

$$\frac{\partial I[|\underline{\psi}_t\rangle]}{\partial a_j^{(i)}} = 0, \quad 1 \leq i \leq M, \; 1 \leq j \leq N, \tag{45}$$

and then using those parameters to determine $I[|\underline{\psi}_t\rangle] > E_0$. Not only is the complete analogy with the one-channel case[19] obvious, but it is also straightforward to show that use, e.g., of (43) in truncated form, leads precisely to the *same* variational result for the energy as in the Goldflam-Kouri procedure,[18] i.e., to the standard Rayleigh-Ritz bound. Hence, this establishes that the variational method will always yield real energies. The results of this section are thus twofold: first, Eq. (7) has been derived variationally, and second, the bound obtained on the energy is seen to be not only real, but identical to that from a standard Rayleigh-Ritz calculation using a trial function formed by $\sum_j|\psi_j\rangle$. Calculations based on these equations are discussed in Sec. III.

5. Choices of W

So far we have presented a general form of the theory, not specifying choices of $\underline{W}$. There are two aspects of such a choice we shall consider here. First is the role of connectedness; second is the kind of approximation that the choice suggests.

Since we are advocating the use of the present method as the $E<0$ extension of CKE procedures for $E>0$, it is clear that the structure of the equations on which the negative-energy calculations are based must be the same as for the positive-energy case. Thus, even though no disconnected graph singularities can ultimately be present in bound-state calculations, the requirement that for $E>0$, $\underline{W}$ be chosen to secure a kernel $\underline{G}_0(+)\underline{V}$ in Eq. (11) having a (finite) connected iterate means that a similar $\underline{W}$ must be chosen for $E<0$. This remark is strongly supported by the only calculations to date which have examined the effect of choosing values of W_{jk} not yielding a connected iterated kernel. This was done for e^-+H scattering, where the approximation of retaining only the ground state of hydrogen in a calculation using the approximation of Sec. II B 4 a above ensured an initially connected structure.[20] Even though any choice of $\underline{W}$ necessarily gives a connected kernel, the best pair of scattering lengths obtained from the calculation was obtained for the (unique) values of W_{11} and $W_{21}=1-W_{11}$ that in the general case yield a connected kernel.

As for those choices of $\underline{W}$ that lead to CKE's, we have so far found only two kinds, the CPA's and the Faddeev-Lovelace (FL) choice, the latter leading[7] to the Faddeev equations ($n=3$) or the Bencze-Redish equations (arbitrary n). The structure of the equations which follow from these two types of choice is very different. In the former case, the role of channel Green's functions $G_j(+)$ and channel interactions V_j is emphasized. In the latter case, the n-body free Green's function $G_0(+)$ and the various (off-shell) $(n-1)$-, $(n-2)$-, . . . , 3-, 2-body T matrices are emphasized. Bound-state approximations to $G_j(+)$ and $|\psi_j\rangle$, as in Sec. II B 4 a, seem best suited to the former case, while pole approximations seem best suited to the latter case *when* the various (off-shell) T matrices are known or can be approximated with reasonable accuracy for the particular problem.[21] Very often, the relevant T matrices are not known, in contrast to the channel interactions V_j, especially in the case of atomic or molecular systems. No general prescriptions for choosing W can be given in advance, although we do note that if the relevant T matrices are known, the FL choice may be easier to work with if either three-body channels or three-body break up states in two-body channels are to be included in the calculations.

6. Comparison with the shell model

We shall consider the shell model as applied in typical nuclear physics calculations.[22] The first point to note is that this model is an example of the present procedure in which j is limited to only one channel: $j=0$, the n-particle breakup channel, for which $\mathrm{H}=H$ and no non-Hermiticity problems occur. It is obvious that in the simplest case, the states of $H_j=H_0$ are the n-particle plane wave states, and so provide a complete expansion set for any system. As is well known, the normal practice is to follow the procedure of Sec. II B 4 b and add to H_0 (and subtract from V_0) a sum of one-body attractive potentials that produce the shell model bound states. The set of bound and continuum states of the one-body potential is still assumed to be complete. Because of this, the model provides an in-principle complete description of all bound states. Hence, it is never necessary to go beyond the shell model. Furthermore, we note that the use of a complete set of states means that the shell model can be used to describe the various channel clusterings discussed in the preceding. Indeed, the near equality of cluster model and shell-model wave functions for light nuclei bear this out.

Given these remarks, the proposal to use the non-Hermitian, many-body methods we are advocating herein may seem no more than an academic exercise, at least for application to nuclear problems. However, the shell model is exact only in principle. For nonlight nuclei, it may be impractical to include the possibly large number of shell-model states needed to describe clustering effects. On the other hand, they enter naturally in the present description. Hence the many-body method we are considering is a complement rather than a rival to the shell model, and ideally would be used to describe few-body clustering (deuterons, alphas, etc.), although its possible application to fission is evident. Shell-model states could be used to describe the bound clusters occurring in the various arrangement channels; the occurrence and coupling of such channels in the bound-state problem is the new aspect of the method we advocate here.

III. APPLICATION TO THE H_2^+ MOLECULAR ION

Equations (6) or (7) would seem to have a natural application to molecular structure, since, in the language of the present approach, the arrangement channel structure of molecules is obvious. In this section, we apply the theory to the simplest molecular system, viz. H_2^+, using the Born-Oppenheimer approximation for the Schrödinger Hamiltonian H and the simplest possible approximations for the three calculational procedures of Sec. II B 4.

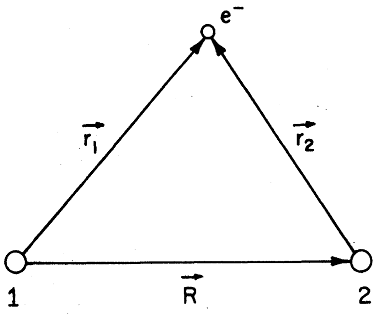

FIG. 2. Coordinates for the H_2^+ system. The protons are labeled 1 and 2.

We shall compare the results with the exact calculations of Wind[23] and also with the results of perturbation theory.[24] As we shall see, our simple (crude) approximations lead to unexpectedly accurate results, particularly in comparison with the well-known results of perturbation theory. These latter results are insufficiently accurate to use the zeroth-order approximate wave function as a model for the structure of H_2^+, another well-known point,[24] and one we return to later. The success of the $e^- + H$ scattering results[14,25] implies that the accuracy of the present H_2^+ calculation is no accident, and this is borne out by further calculations for H_2^+ using larger bases.[26] The extension of the $e^- + H$ scattering results to negative energies (i.e., the affinity of H^-), discussed by Levin,[27] is a further indication of the power of the method.

A. Comparison calculations

The H_2^+ system, with the various interparticle coordinates labeled, is shown in Fig. 2. In the Born-Oppenheimer approximation,[24] the Hamiltonian H for the system is

$$H = H_0 - e^2/r_1 - e^2/r_2 + e^2/R \ , \tag{46}$$

where H_0 is the electron kinetic energy operator. The Schrödinger eigenvalue equation is

$$H\,|\Psi(R)\rangle = E(R)\,|\Psi(R)\rangle \ , \tag{47}$$

so that one determines an energy "surface" $E(R)$. Assuming $E(R)$ to display a minimum at $R = R_{eq}$, the total electronic binding energy is given by $E(R_{eq})$, where we have $(\partial E/\partial R)_{R_{eq}} = 0$.

It is well known that H is separable in confocal elliptic coordinates[4,23] so that a numerically exact solution for $E(R)$ and $|\Psi(R)\rangle$ can be obtained and R_{eq} and $E(R_{eq})$ then determined. The values of R_{eq}, $E(R_{eq})$, and the spectroscopic dissociation energy $D_e = E(R_{eq}) - e^2/2a_0$ as calculated by Wind[25] are given in Table I.

The H_2^+ system has also been used as a testing ground for various approximations. One of the simplest is degenerate perturbation theory. (This gives the same result as a corresponding variational treatment.[28]) The idea is to regard H_2^+ as made up of hydrogen and a proton in two different ways (just the channels we shall consider in the next subsection, although the dynamics is not the same). To first order, the wave function is a linear combination of the degenerate hydrogenic states centered on each proton:

$$|\Psi(R)\rangle \equiv |\Psi\rangle \cong |\Psi^{(0)}\rangle = C_1\,|\eta_{1s}(1)\rangle + C_2\,|\eta_{1s}(2)\rangle \ , \tag{48}$$

where the C_i are R-dependent constants to be determined and $|\eta_{1s}(i)\rangle$ is the hydrogenic ground state (centered on proton i).

Both the $C_i(R)$ and $E(R)$ are determined by solving a secular equation, the details of which are given for example by Pilar.[4] Two solutions are obtained, corresponding to bonding and antibonding orbitals. We are only interested in the former solution here, the dissociation energy curve $D_e(R)$ for which is given by[4]

$$D_e(R) = (\alpha + \beta)/(1 + \Delta) \ .$$

In this equation, α and β are[4]

$$\begin{aligned}\alpha &\equiv \langle\eta_{1s}(1)\,|\,-\frac{e^2}{r_1} + \frac{e^2}{R}\,|\eta_{1s}(2)\rangle \\ &= 2\epsilon_{1s}\left(1 + \frac{1}{R}\right)e^{-2R}\end{aligned} \tag{49}$$

and

$$\begin{aligned}\beta &\equiv \langle\eta_{1s}(1)\,|\,-\frac{e^2}{r_2} + \frac{e^2}{R}\,|\eta_{1s}(2)\rangle \\ &= 2\epsilon_{1s}\left((1+R)e^{-R} - \frac{\Delta}{R}\right) \ ,\end{aligned} \tag{50}$$

where $\epsilon_{1s} = -e^2/2a_0$, while Δ is given by

$$\begin{aligned}\Delta &\equiv \langle\eta_{1s}(1)\,|\,\eta_{1s}(2)\rangle \\ &= (1 + R + \tfrac{1}{3}R^2)e^{-R}\end{aligned} \tag{51}$$

and all distances are measured in units of a_0. We

TABLE I. Comparison of H_2^+ ground-state energies and equilibrium separations.

	R_{eq}	$E(R_{eq})$ (eV)	D_e (eV)
Exact calculation	$2.02a_0$	−16.39	−2.79
Perturbation calculation (Schrödinger equation)	$2.50a_0$	−15.39	−1.78
Channel-coupling array calculation	$2.07a_0$	−16.67	−3.07

note here that the nonorthogonality overlap $\Delta(R)$ occurs in the denominator of $D_e(R)$ essentially because $|\Psi\rangle$ is being expanded in a basis of nonorthogonal functions. [As we shall see, this denominator does not even enter the calculation of $D_e(R)$ using the projection technique method, i.e., just as in $E>0$ calculations,[5] the nonorthogonality of different channel functions is finessed.]

The results[4] of this calculation are also given in Table I. It is seen that $E(R_{eq})$ and R_{eq} are accurate to within 7 and 25%, respectively, while D_e is accurate only to within 36%. The fact that $E(R_{eq})$ is better than a factor of three more accurate than R_{eq} is an indication of the usual result that energies can be more accurately determined than wave functions perturbatively, and R_{eq} must reflect this, being dependent on the electron density. A rather different result occurs for the channel component calculation, as shown below.

In addition to the results discussed here, i.e., the bonding orbital for which $C_1=C_2=[2(1+\Delta)]^{-1/2}$, both the exact and approximate calculations yield a second state, for which there is no bonding. This has $C_1=C_2=[2(1-\Delta)]^{-1/2}$, detailed potential energy surfaces for which are given in Ref. 4.

The perturbation/variation result is the simplest approximation to the exact result, and many others have been used. The next simplest, which employs only a 1s function but includes a scale parameter, leads to an improvement in D_e of 0.5 eV, and other calculations achieve much better accuracy.[4] We only consider the simplest of approximations here because it is the one, despite its poor values of D_e and R_{eq}, that is used as a basis for introducing the molecular orbital method used for more complex molecules. As we shall see, the arrangement channel procedure leads to much better results for D_e and R_{eq}, with what is apparently an identical wave function. The question of an identical wave function is one of interpretation, which we discuss in Sec. D below.

B. Channel component calculations

We consider here only the simplest approximate calculations; these use just the hydrogenic ground state $|\eta_{1s}\rangle$ as in the preceding, but with vastly different results. We also remark that molecular systems are almost ideally suited for the method we are discussing here, since by its very structure of bound atoms, the channel nature of the system is obvious. Thus H_2^+, being the simplest molecule, is a likely system to be well described by the many-body arrangement channel methods. Indeed, it is a test case in the sense that we must do at least as well as the more standard methods in describing the molecule, when comparable approximations are used. The results described below clearly indicate that the method is successful.

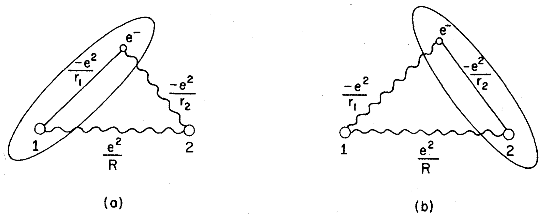

FIG. 3. The two 2-body partitions of the H_2^+ system: (a) corresponds to channel 1 and (b) to channel 2. Binding interactions are indicated by solid lines and channel interactions by wavy lines, while the bound clusters are enclosed by the large ovals.

1. Projection technique

For H_2^+ there are two channels, denoted (1) and (2), and defined by which proton binds the electron:

$(1,e^-)+2$, channel (1);

$(2,e^-)+1$, channel (2);

where (,) means a bound pair. These two channels are represented schematically in Fig. 3 along with the relevant interactions. From this diagram plus the definitions of the two channels, we see that

$$H_1=H_0-\frac{e^2}{r_1}\,,\quad V_1=-\frac{e^2}{r_2}+\frac{e^2}{R} \tag{52}$$

and

$$H_2=H_0-\frac{e^2}{r_2}\,,\quad V_2=-\frac{e^2}{r_1}+\frac{e^2}{R}\,. \tag{53}$$

The partitionings (52) and (53) are to be used in Eq. (7). In order to apply this system, we must specify $\underline{W}$. Since this is a two-channel problem, $\underline{W}$ is a 2×2 matrix, and we choose it to be the CPA obtained by first setting $l=k$ in $W_{jl}V_k$ and then selecting $W_{jj}=0$ and $W_{jk}=1$, $j\neq k$:

$$\underline{W}=\begin{pmatrix}0&1\\1&0\end{pmatrix}.$$

This value of $\underline{W}$ is the same as used in the $e^-+\mathrm{H}$ calculations,[20,25] and clearly obeys[5] $\sum_j W_{jk}=\sum_k W_{jk}=1$. Equation (7) thus becomes

$$\begin{pmatrix}H_1&V_2\\V_1&H_2\end{pmatrix}\begin{pmatrix}|\psi_1\rangle\\|\psi_2\rangle\end{pmatrix}=E\begin{pmatrix}|\psi_1\rangle\\|\psi_2\rangle\end{pmatrix}. \tag{54}$$

According to the discussion in Sec. II, $|\psi_j\rangle$ describes the system exactly when r_j (in this case R) is asymptotic. From (52) or (53), this means that when $R\to\infty$, $|\psi_j\rangle=a_\alpha(j)\,|\eta_\alpha(j)\rangle$, where α denotes a hydrogenic state and $a_\alpha(j)$ is a constant to be determined. Since the lowest state has $\alpha=1s$, we use this one-state approximation, although we expect that for R near to R_{eq}, $|\psi_j\rangle = \sum_\alpha a_\alpha(j)|\eta_\alpha(j)\rangle$. Hence, our projection approximation [i.e., Eq. (24)] involves

$$|\tilde{\psi}_j\rangle \equiv P_j|\psi_j\rangle = |\eta_{1s}(j)\rangle\langle\eta_{1s}(j)|\sum_\alpha a_\alpha(j)\eta_\alpha(j)\rangle$$

$$= a_{1s}(j)|\eta_{1s}(j)\rangle \equiv a_j|\eta_{1s}(j)\rangle . \qquad (55)$$

With this approximation, $|\tilde{\Psi}\rangle$ now becomes

$$|\tilde{\Psi}\rangle = a_1|\eta_{1s}(1)\rangle + a_2|\eta_{1s}(2)\rangle \equiv |\Psi^{(0)}\rangle , \qquad (56)$$

where $|\Psi^{(0)}\rangle$ is given by Eq. (48). [Normalization alone will imply that the a_i of Eq. (56) and C_i of Eq. (48) are equal.] So the first point we see is that the projection approximation leads to the *same* approximation to $|\Psi\rangle$ as in the usual approximation to the Schrödinger equation. The dynamics, as we have stressed above, is not the same however.

Since $P_j = |\eta_{1s}(j)\rangle\langle\eta_{1s}(j)|$, the approximate form of (54), viz. Eq. (24), becomes for this case

$$\begin{pmatrix} \epsilon_{1s} - E(R) & \langle\eta_{1s}(1)|V_2|\eta_{1s}(2)\rangle \\ \langle\eta_{1s}(2)|V_1|\eta_{1s}(1)\rangle & \epsilon_{1s} - E(R) \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0 , \qquad (57)$$

where $\epsilon_{1s} = -e^2/2a_0 = -13.6$ eV is the ground-state energy of the H atom. Note that no nonorthogonality overlaps occur in this equation, nor will they occur if more elaborate expansions for $|\psi_j\rangle$ are used. The two matrix elements in (57) occurring as off-diagonal elements are equal and are given by

$$M(R) \equiv \langle\eta_{1s}(1)|V_2|\eta_{1s}(2)\rangle$$

$$= 2\epsilon_{1s}\left(\frac{2R}{3} - \frac{1}{R}\right)e^{-R} \equiv \beta , \qquad (58)$$

with R measured in units of a_0 and β given by Eq. (50). The energies are given by

$$E^{\pm}(R) = \epsilon_{1s} \pm M(R) , \qquad (59)$$

so that the spectroscopic dissociation energy D_e for the bonding state is

$$D_e = M(R_{eq}) . \qquad (60)$$

Differentiating (58) leads to bonding for $E^{+}(R)$, with a minimum at $R_{eq} = 2.07\ a_0$, implying $E(R_{eq}) = -16.67$ eV and $D_e = -3.07$ eV. This is an accuracy of 2% for R_{eq} and $E(R_{eq})$ and of 10% for D_e as compared to the corresponding exact results. The comparison of all three calculations is given in Table I. (We also obtain $a_1 = \pm a_2 = [2(1\pm\Delta)]^{-1/2}$ for the bonding (+) and nonbonding (−) cases.) We thus find that the channel-component method leads to results three times more accurate than the perturbation/variation approximate results for the Schrödinger equation using the same approximation for $|\Psi\rangle$, but, of course, different dynamics. Note that because of the simplicity of the approximation (55), (54) has reduced to the Hermitian matrix equation (57). Also, $|\tilde{\psi}_j\rangle$ of (55) has a well-defined phase under T. This latter feature must be retained in a more elaborate calculation, but hermiticity of $\underline{\mathrm{H}}$ need not be.

Let us now consider this calculation in more detail. Not only are the equilibrium values in very good agreement with the exact ones, so are the values of $D_e(R)$ for all R, as shown in Fig. 4. A similar comparison of the perturbation/variation results for $D_e(R)$ with that of the channel-component calculations is given in Fig. 5. This latter figure is of greater interest to us than Fig. 4, since the results shown in Fig. 5 correspond to the *same* wave function but different dynamics. Each curve in Fig. 5 is composed of two contributions, the perturbation/variation result being given by the sum of $\alpha/(1+\Delta)$ and $\beta/(1+\Delta)$ as above, while $D_e(R)$ [$=M(R)$ of Eq. (60)] for the channel-component case is given by

$$M(R) = \langle\eta_{1s}(1)|-\frac{e^2}{r_1}|\eta_{1s}(2)\rangle + \langle\eta_{1s}(1)|\frac{e^2}{R}|\eta_{1s}(2)\rangle$$

$$\equiv 2\epsilon_{1s}(1+R)e^{-R} - 2\epsilon_{1s}\frac{\Delta}{R} . \qquad (61)$$

In contrast to the binding energy term

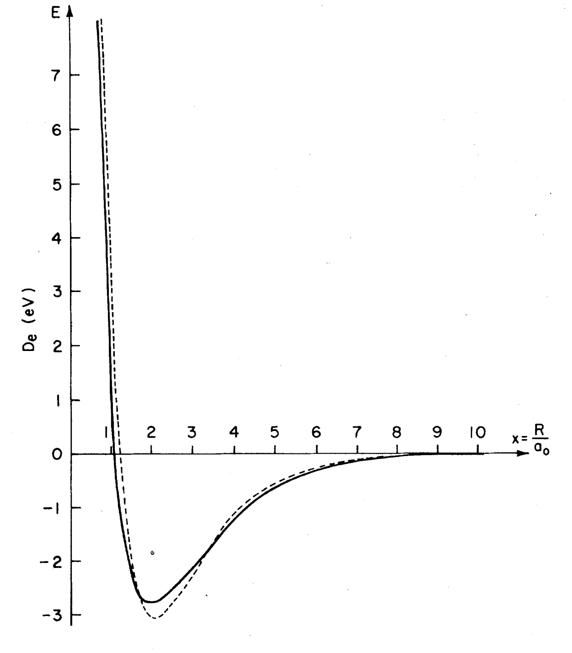

FIG. 4. Variation of the dissociation energy $D_e(R) = E^{+}(R) - \epsilon_{1s}$ with internuclear separation $x = R/a_0$. Solid line, exact result; dashed line, the channel-coupling array approximate result.

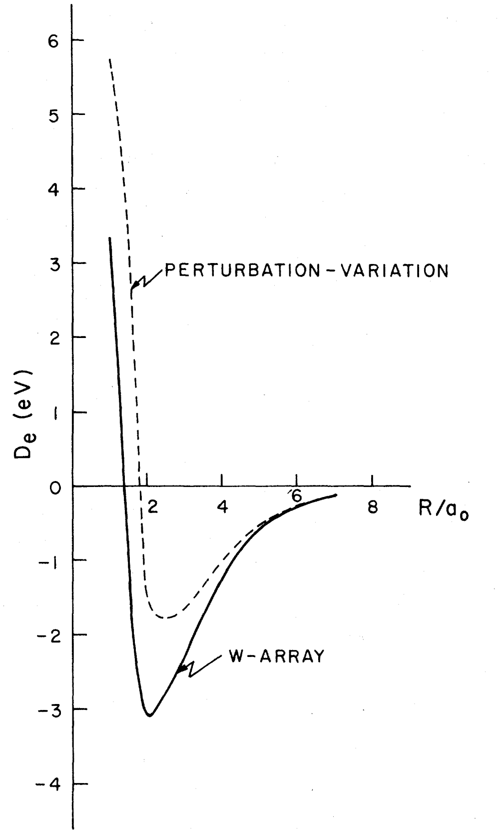

FIG. 5. Comparison of the dissociation energy curves from the channel-coupling array calculation (solid line) and the perturbation/variation result (dashed line).

$2\epsilon_{1s}\langle\eta_{1s}(i)|r_i^{-1}|\eta_{1s}(i)\rangle$ occurring in the H-atom energy, the factor $2\epsilon_{1s}\langle\eta_{1s}(1)|r_1^{-1}|\eta_{1s}(2)\rangle$ has the appearance of an exchange term. This interpretation is not the one we prefer. Instead we regard

$$\langle\eta_{1s}(1)|r_1^{-1}|\eta_{1s}(2)\rangle \propto \langle\psi_1|r_1^{-1}|\psi_2\rangle$$

as the attractive (binding) part of the channel 1–channel 2 interaction. Indeed, it can be regarded as the "channel averaged" attraction of the electron on one site to the proton on the other. Similarly, the term

$$\langle\eta_{1s}(1)|R^{-1}|\eta_{1s}(2)\rangle \propto \langle\psi_1|R^{-1}|\psi_2\rangle$$

is the repulsive part of the channel 1–channel 2 interaction corresponding to the channel averaged proton-proton repulsion. The interplay (i.e., difference) of these two terms is responsible for binding (or nonbinding) in the present approximation.

This latter remark is extremely important. By construction, the correction to the energy of the "free" channel state, which is just the ground-state energy of hydrogen, is given by $M(R) = D_e(R)$. In terms more appropriate to the perturbation/variation calculation of the preceding subsections, the zeroth-order approximation to the energy is determined from a pair of noninteracting $H + H^+$ systems. Hence, to obtain the correct dissociation energy, we must produce an accurate evaluation of $\langle\psi_1|r_1^{-1} - R^{-1}|\psi_2\rangle$, i.e., the approximation $|\psi_i\rangle \approx |\tilde{\psi}_i\rangle$ of (55) must give a relatively accurate estimate of the preceding matrix element. As shown in Fig. 6, the two terms of (61) contributing to $D_e(R)$ in the present calculation are each of large magnitude for R in the region $1 \leq R \leq 7$, exactly as in the case of the perturbation/variation approach. We find for example that the two terms of Eq. (61) have the values -10.5 and 7.44 eV for $R = R_{eq}$.

Hence, to obtain $D_e(R)$ shown in Figs. 4 or 5, where the magnitudes are small for $1 \leq R \leq 7$, it is necessary to take the difference of two relatively large numbers. In order for $D_e(R)$ to be accurate in this range of R, *each* of the two large magnitudes must therefore be accurately determined. It is evident that the arrangement channel method produces this result, and more accurately than in the perturbation/variation approach. As a consequence, we believe that Eq. (56) represents an accurate approximation to $|\Psi\rangle$, although only if it is regarded as a *channel-component* approximation and not as either the usual variational or degenerate-perturbation-zeroth-order wave function. We shall enlarge on this comment in Sec. D below.

Apart from noting the relatively high accuracy of the results, we remark on two other points. First, we see that the accuracy of R_{eq} is a dynamical consideration and is not dependent on the accuracy of the approximation to $|\Psi\rangle$. Second, since relatively crude input [Eq. (55)] has led to relatively quite accurate output, we may ask why this has occurred. One way of understanding of this point is as follows. Returning to Eq. (57) we may solve for a_2 in terms of a_1, yielding

$$E(R) = \epsilon_{1s} + \frac{\langle\eta_{1s}(1)|V_2|\eta_{1s}(2)\rangle\langle\eta_{1s}(2)|V_1|\eta_{1s}(1)\rangle}{E(R) - \epsilon_{1s}}, \tag{62}$$

or in operator form,

$$E|\psi_1\rangle = H_1|\psi_1\rangle + V_2(E - H_2)^{-1}V_1|\psi_1\rangle, \tag{63}$$

with a similar result for $|\psi_2\rangle$.

Equation (63) is perhaps more suggestive than Eq. (62). First, we see that when $|\psi_1\rangle$ is approximated by $|\tilde{\psi}_1\rangle$, the correction to the result $E \cong \langle\psi_1|H_1|\psi_1\rangle$ is of second order in the channel interactions, with a bound-state propagator. This is analogous to the result involving Lippmann's identity[5,7] for the $E > 0$ case, except of course that when $E > 0$, Lippmann's identity cannot be directly used,

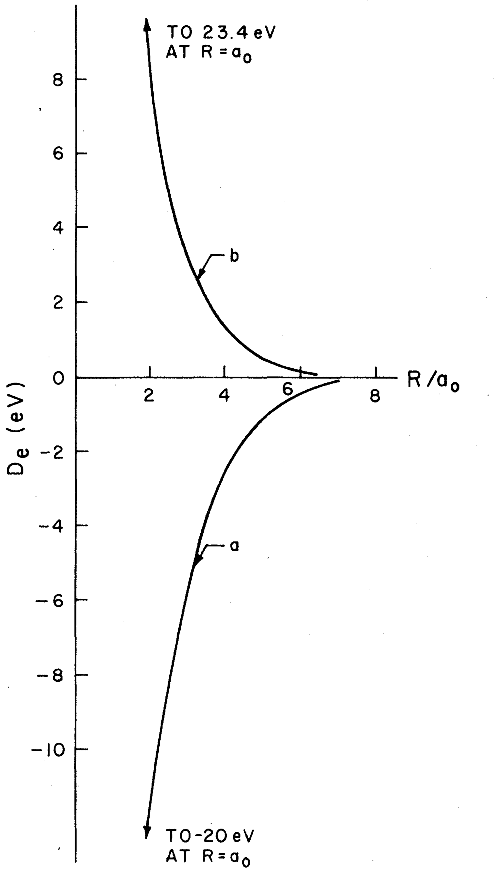

FIG. 6. R dependence of the various contributions to $D_e(R)$ shown in Fig. 5. Curve (a) is the channel averaged electron-proton attraction $2\epsilon_{1s}\langle\eta_{1s}(1)|r_1^{-1}|\eta_{1s}(2)\rangle$, while curve (b) is the channel-averaged proton-proton repulsion $-2\epsilon_{1s}\langle\eta_{1s}(1)|R^{-1}|\eta_{1s}(2)\rangle$.

since no approximation $|\tilde{\psi}_1\rangle$ can be expected to correspond to the eigenvalue of interest. Nevertheless, since the "interaction" acts twice, the result could be more accurate than obtained from ordinary perturbation theory. The assumption here is that a sufficiently accurate single state approximation to $|\psi_1\rangle$ leads to a value of E relatively stable against departures from this approximation, so that (63) behaves like a second-order accurate result. Furthermore, we note that both (62) and (63) involve the eigenvalue E nonlinearly, in a form analogous to the second-order Brillouin-Wigern perturbation result. As noted for example by Baym,[15] solution of such a nonlinear equation may provide a much more accurate result than using ordinary Rayleigh-Ritz perturbation theory, and is clearly doing so here. We also note that while Eq. (63) is generalizeable in the case of N channels to

$$E|\psi_1\rangle = H_1|\psi_1\rangle + \prod_{j=2}^{N} V_j(E-H_j)^{-1}V_1|\psi_1\rangle ,$$

one should not expect that a single state approximation in each channel will produce a result of Nth order stability, because it is highly unlikely that a single state can be a good approximation in a many-channel situation.

2. Perturbation theory

We first write the $\underline{H}$ of Eq. (54) in the form

$$\underline{H} = \begin{pmatrix} H_1 & 0 \\ 0 & H_2 \end{pmatrix} + \begin{pmatrix} 0 & V_2 \\ V_1 & 0 \end{pmatrix}$$

$$\equiv \underline{H}_0 + \underline{V} . \tag{64}$$

From (52) and (53), it is clear that $\underline{H}_0$ will bind, so that introduction of the auxiliary potentials $\underline{U}$ of Eqs. (28) and (29) is unnecessary. In fact, the unperturbed solutions $|\underline{\chi}\rangle$ of $\underline{H}_0$ contain just the eigenstates of hydrogen. Since we seek the ground state of H_2^+ we choose $|\underline{\psi}^{(0)}\rangle$ of (31) to be

$$|\underline{\psi}^{(0)}\rangle = |\underline{\chi}_{1s}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} |\eta_{1s}(1)\rangle \\ |\eta_{1s}(2)\rangle \end{pmatrix} , \tag{65}$$

so that $E^{(0)} = \epsilon_{1s}$. From Eq. (32), the first-order correction to $E^{(0)}$ is given by

$$E^{(1)} = \langle \underline{\chi}_{1s} | \underline{V} | \underline{\chi}_{1s} \rangle$$

$$\equiv M(R) , \tag{66}$$

where $M(R)$ is given by Eq. (55). Hence, to first order,

$$E(R) = \epsilon_{1s} + M(R) ,$$

which is just the form found in the preceding subsection that led to bonding. Clearly, the same values of R_{eq}, $E(R_{eq})$ and D_e result, thus establishing that first-order perturbation theory and the crudest form of the projection method lead to identical bonding results.

3. Variational method

We shall apply the procedure described in subsection 3c of Sec. II B to the H_2^+ system using as a trial vector the quantity $|\underline{\psi}_t\rangle$ given by

$$|\underline{\psi}_t\rangle = \begin{pmatrix} a_1 |\eta_{1s}(1)\rangle \\ a_2 |\eta_{1s}(2)\rangle \end{pmatrix} . \tag{67}$$

Then the trial state vector $|\underline{\Psi}_t\rangle$ is

$$|\underline{\Psi}_t\rangle = \begin{pmatrix} |\Psi_t\rangle \\ |\Psi_t\rangle \end{pmatrix} , \tag{68}$$

with

$$|\Psi_t\rangle = a_1\,|\eta_{1s}(1)\rangle + a_2\,|\eta_{1s}(2)\rangle \ , \tag{69}$$

the same as in the preceding sets of calculations. The quantities a_1 and a_2 are the variational parameters to be determined from Eqs. (41), (42), and (44) using $|\underline{\mathrm{f}}\rangle = |\underline{\psi}_t\rangle$ and $|\underline{\mathrm{F}}\rangle = |\underline{\Psi}_t\rangle$. This must yield (Sec. IIB 4 c) the results of Sec. IIIA.

Using the preceding identifications, and substituting into $I[\,|\underline{\psi}_t\rangle\,]$ of Eq. (41), we find

$$I[\,|\underline{\psi}_t\rangle\,] = \frac{N(a_1, a_2, R)}{D(a_1, a_2, R)} \ ,$$

where

$$N(a_1, a_2, R) = (a_1^2 + a_2^2)(\epsilon_{1s} + \langle \eta_{1s}(1)\,|\,V_1\,|\,\eta_{1s}(1)\rangle) + 2a_1a_2[\epsilon_{1s}\Delta + M(R)\,]$$

and

$$D(a_1, a_2, R) = a_1^2 + a_2^2 + 2a_1a_2\Delta \ ,$$

with $M(R)$ given by Eq. (58), while $\underline{\mathrm{H}}$ and its partitions are given in subsection 1 above. The overlap $\langle \eta_{1s}(1)\,|\,\eta_{1s}(2)\rangle = \Delta(R)$ is given by Eq. (51), while $\langle \eta_{1s}(1)\,|\,V_1\,|\,\eta_{1s}(1)\rangle = \langle \eta_{1s}(2)\,|\,V_2\,|\,\eta_{1s}(2)\rangle$, is just the quantity α of Eq. (49).

From Eq. (45) it is straightforward to derive the result that $a_1^2 = a_2^2$ or

$$a_1 = \pm a_2$$

as expected. This then leads to two solutions for $I[\,|\psi_t\rangle\,] \equiv E^{\pm}(R)$:

$$E^{\pm}(R) = \epsilon_{1s} + \frac{\alpha \pm M(R)}{1 \pm \Delta} \ . \tag{70}$$

If we now recall the identity of β of Eq. (50) and $M(R)$, we see that Eq. (68) is *identical* to the result obtained for the energy using either degenerate perturbation theory[4] or the variational method[20] as applied to the Schrödinger equation and discussed in subsection A of this section. That is, Eq. (70) leads to $R_{eq} = 2.50a_0$ and $E^{+}(R_{eq}) = -15.98$ eV, which is of course an upper bound to the energy. This exemplifies the general result (II B 4 c) that the many-body variational procedure of Eqs. (41)–(44) leads to precisely the same results as the usual Rayleigh-Ritz procedure. Since $|\underline{\psi}_t\rangle$ was chosen to have such simple form, it is perhaps not too surprising that the diagonalization procedure of Sec. B 1 produces a more accurate result.

C. Symmetry effects

Thus far we have not taken account of the identity of the two protons in the H_2^+ molecule. We now consider this symmetry property, showing that it can be used to decouple the pair of equations represented by (54). The method used is similar to that described elsewhere for the identical particle problem.[29]

Written out in detail, (54) becomes

$$H_1\,|\psi_1\rangle + V_2\,|\psi_2\rangle = E\,|\psi_1\rangle \tag{71}$$

and

$$H_2\,|\psi_2\rangle + V_1\,|\psi_1\rangle = E\,|\psi_2\rangle \ . \tag{72}$$

Let P_{12} denote the two-particle transposition operator, which changes label 1 into 2 and vice versa. From (52) and (53) it follows that

$$P_{12}H_jP_{12} = H_k \ \text{ and } \ P_{12}V_jP_{12} = V_k, \ \ j \neq k \ .$$

Applying $\pm P_{12}$ from the left to both sides of (72), and using the above results, we find

$$\pm H_1\ P_{12}\,|\psi_2\rangle \pm P_{12}V_1\ \,|\psi_1\rangle = \pm EP_{12}\,|\psi_2\rangle \ , \tag{73}$$

while (71) can be reexpressed as

$$H_1\ \,|\psi_1\rangle \pm (P_{12}V_1)(\pm P_{12}\,|\psi_2\rangle) = E\,|\psi_1\rangle \ , \tag{74}$$

where we have repeatedly used $P_{12}P_{12} = 1$.

On adding (73) to (74) we find

$$(H_1 \pm P_{12}V_1)\,|\psi^{\pm}\rangle = E\,|\psi^{\pm}\rangle \ , \tag{75}$$

where

$$|\psi^{\pm}\rangle = \,|\psi_1\rangle \pm P_{12}\,|\psi_2\rangle \ . \tag{76}$$

Equation (75) is equivalent to the pair (54), except that the effect of proton identity has been made explicit. This is obvious from the presence of the exchange term $P_{12}V_1$. Had we initially introduced the spin of the protons, then the + (−) factor could easily be shown to correspond to singlet (triplet) spins, exactly as in $e^- + H$ scattering.[20,25] In fact, this reduction of (51) to (73) is identical to the analogous procedure in the positive energy case, except that when $E < 0$, one cannot make use of Lippmann's identity[5,7] $G_j(+)(V_k - V_j) = 1 - \delta_{kj}$ to show that a perturbative solution to (73) contains matrix elements of V_1, since Lippmann's identity is not valid in this case, as noted above.

The presence of H_1 in (75) implies that $|\psi^{\pm}\rangle$ is to be expanded in eigenstates of the h_1 operator [see Eqs. (2) and (3)]. In the present case this means that we have ($h_1 = H_1$)

$$|\psi^{\pm}\rangle = \sum_{\alpha} a_{\alpha}^{\pm}\,|\eta_{\alpha}(1)\rangle \ . \tag{77}$$

Substitution of (77) into (75) eventually leads to the infinite set of coupled equations

$$[\,\epsilon_{\alpha} - E(R)\,]a_{\alpha}^{\pm} \pm \sum_{\beta} \langle \eta_{\alpha}(1)\,|P_{12}V_1\,|\,\eta_{\beta}(1\rangle a_{\beta}^{\pm} = 0 \ .$$

Noting that

$$P_{12}V_1\,|\eta_{\beta}(1)\rangle = V_2\,|\eta_{\beta}(2)\rangle \ ,$$

we finally find

$$[\epsilon_\alpha - E(R)]a_\alpha^\pm \pm \sum_\beta \langle \eta_\alpha(1)\,|\,V_2\,|\,\eta_\beta(2)\rangle a_\beta^\pm = 0 \ . \tag{78}$$

Solution of this pair ($\pm$) of equations will yield the eigenstates and eigenvalues of the H_2^+ system in Born-Oppenheimer approximation when V_2 is given by Eq. (53).

To make contact with the work of subsection B1, we truncate the expansion (77), limiting α to $1s$ only [i.e., we use the projection technique of Sec. IIB4a, with $P_1 = |\eta_{1s}(1)\rangle\langle\eta_{1s}(1)|$]. Then (78) becomes

$$\epsilon_{1s} - E(R) \pm \langle \eta_{1s}(1)\,|\,V_2\,|\,\eta_{1s}(2)\rangle = 0$$

or

$$E^\pm(R) = \epsilon_{1s} \pm M(R) \ , \tag{79}$$

where $M(R)$ is given by (58). It is clear that (79) is precisely the same solution for $E^\pm$ as obtained by solving the projected pair or Eqs. (57).

Not only do we find values for $E^\pm(R)$, we can also recover the original components $|\psi_1\rangle$ and $|\psi_2\rangle$. We have

$$|\psi_1\rangle \pm P_{12}\,|\psi_2\rangle = a^\pm\,|\eta_{1s}(1)\rangle \ .$$

Solving these equations for $|\psi_1\rangle$, $j = 1, 2$, we get

$$|\psi_1\rangle = (a^+ + a^-)\,|\eta_{1s}(1)\rangle \equiv a_1\,|\eta_{1s}(1)\rangle$$

and

$$P_{12}\,|\psi_2\rangle = (a^+ - a^-)\,|\eta_{1s}(1)\rangle \ . \tag{80}$$

But since $P_{12}P_{12} = 1$, (80) becomes

$$|\psi_2\rangle = (a^+ - a^-)\,|\eta_{1s}(2)\rangle \equiv a_2\,|\eta_{1s}(2)\rangle \ ,$$

thus recovering the equations for the $|\psi_j\rangle$ used in the original projection approximation of subsection B1. Furthermore, the requirement that $P_{12}|\Psi\rangle = \pm\,|\Psi\rangle$ leads to $a_1 = \pm a_2$, thus completely determining the solution for $|\Psi\rangle$.

In addition to the projection calculation just noted, one could also carry out perturbation and variational calculations, or could even attempt to solve (75) directly using confocal elliptic coordinates, although in the present case this would simply duplicate the extensive and detailed numerical work already in existence.[24] Our point, however, has not been to consider a further set of calculations that would duplicate existing results, but to indicate how the effects of symmetry reduce the pair of equations (54) to a single equation with an exchange term. It is clear that similar techniques are available for general identical particle problems.

D. Conclusions

1. Interpretation of the wave function

In Sec. IIIB1 we concluded that the wave function (56), identical to the perturbation/variation wave function (48), was a good approximation to the actual Schrödinger wave function for the H_2^+ system. This conclusion is based on the relatively high accuracy of the arrangement channel calculations, as indicated in Table I and Fig. 4. Since this accuracy is in sharp contrast to that based on results of a standard quantum-mechanical calculation using an identical wave function, an explanation of this apparent paradox is obviously required.

We indicated above that the explanation for these two disparate sets of results is to be found in interpretation of the wave function. Let us consider the usual approach first. In either the perturbation or the variation method for the Schrödinger equation, one can write $|\Psi\rangle$ as a linear combination of states centered on each of the protons, $|\eta_\alpha(i)\rangle$. The nonorthogonality of $|\eta_\alpha(1)\rangle$ and $|\eta_\beta(2)\rangle$, $\alpha \neq \beta$, is a well-known feature of such an expansion, and is a reflection of the fact that an expansion of the form $|\Psi\rangle = \sum_\alpha [C_\alpha\,|\eta_\alpha(1)\rangle + D_\alpha\,|\eta_\alpha(2)\rangle]$ is overcomplete. If only $\alpha = 1s$ is retained in the sum, one obtains a simple model of the system, but which predicts observables only poorly when a perturbation or variation calculation, based on the Schrödinger equation, is performed. The standard conclusion is that the simple model is poor. Improved wave functions lead to much more accurate values for R_{eq} and D_e, but imply models whose representation in physical terms is less straightforward. Nowhere in any of these calculations does a description in terms of the different arrangements occur, although one can impose such an interpretation in light of the results of this paper.

Now consider the arrangement-channel approach. In this approach, $|\Psi\rangle$ is no longer obtained by solving the Schrödinger equation approximately. Instead, $|\Psi\rangle$ is approximated by a sum of terms that approximately solve the W-array equations. That is, one first expresses $|\Psi\rangle$ as a sum of contributions from the various channels, i.e., as a sum of components along the axes of a nonorthogonal vector space, the arrangment-channel vector space. If approximations enter at all at this stage, it is through neglect of some channels in the sum on j in Eq. (5). The procedures for determining the components $|\psi_j\rangle$ are as discussed in Sec. IIB, and of course represent a different dynamics for the system. It is in the calculation of the $|\psi_j\rangle$ that approximations are introduced; these are then reflected back in the final form of the wave function, since $|\Psi\rangle$ is given by the sum of the (approximate) $|\psi_j\rangle$'s.

The key to the "interpretation" resolution of the above "paradox" is given in the preceding paragraph. In the standard quantum-mechanical approach, the wave function is expanded in some way and a Schrödinger-like calculation is carried out. In the arrangement-channel approach, the nonorthogonal, channel-vector-space character of $|\Psi\rangle$ is introduced first and a well-defined, non-Schrödinger-like dynamical procedure is then followed to determine the observables. Any approximations are basically introduced for the various channel components directly. The state $|\Psi\rangle$ is finally given by the sum of the various components $|\psi_j\rangle$, and at this stage, the channel nature of $|\Psi\rangle$ is submerged, although this nature is evident in possibly different values of observables. But, within the context of the *dynamical calculations*, the channel components *are* distinguished. Finally, and most importantly, we see that while the approximate solution $|\tilde{\Psi}\rangle$ does not solve the Schrödinger equation, neither does the approximate solution $|\Psi^{(0)}\rangle$. The state $|\tilde{\Psi}\rangle$ is obtained by one dynamical procedure, and the state $|\Psi^{(0)}\rangle$ by another. Both are approximations to $|\Psi\rangle$, and it is clear that the procedure leading to $|\tilde{\Psi}\rangle$ is superior to that giving $|\Psi^{(0)}\rangle$ because it leads to more accurate values of the observables. It therefore follows that $|\Psi\rangle$ is well approximated by $|\tilde{\Psi}\rangle$ in an arrangement-channel quantum sense, but is not well approximated by $|\Psi^{(0)}\rangle$ in a standard quantum-mechanical sense. Clearly, it is essential to couple the dynamics with the ultimate wave function in asking if it is a good approximation.

We cannot emphasize the preceding comment too strongly: in any approximate calculation, one should not remark on the accuracy of a wave function alone. One should also note the calculational procedure and even the observables which have been used to assess the validity of the approximate wave function. While one observable may be accurate, another could be poor. The present calculation is a case in point, since it fails to yield an antibonding energy curve: the *nonbinding* result $E^-(R)$ has a grossly incorrect behavior as $R \to 0$. However, addition of the $2s$ or $2p_0$ state *does* lead to an antibonding solution while maintaining the bonding one,[26] as we shall show in detail in subsequent work.

Since the validity of the channel interpretation of the wave function is so closely linked with the accuracy of the observables calculated, a few additional comments on accuracy are appropriate here. First, there are theoretical grounds, in contrast to the technical details of a particular calculation as per Sec. III B 2, for anticipating accuracy from the channel-coupling method. We argue in analogy to the positive-energy case, as follows. The exact, one-channel scattering amplitude ($E > 0$) can be calculated either from plane wave matrix elements of the t operator or from a matrix element involving the interaction and the exact wave function.[15] The $E < 0$ calculational procedure of this article is analogous to the former procedure. In particular, low-order on-shell approximations to the exact two-body channel-coupling transition operator will lie in between the Born approximation and the full amplitude, and will contain at least second-order (rearrangement) Born terms.[5] Clearly, plane wave matrix elements of such approximations could be more accurate than those of the Born approximation alone. The methods we advocate here are $E < 0$ continuations of the preceding and have the same possibilities inherent in them for producing accuracy as do the $E > 0$ approximation just noted.

Second, we note that the projection/diagonalization technique of Sec. II B 4 a is not a variational procedure. Therefore, adding an extra state into the projection operators P_j of (22) need not give an improved result. In particular, since the complexity of the calculation rapidly increases with the number of channels, we should not be surprised if we find anomalies compared to more standard methods of procedure. For example, we might find that using the ground states in channels 1 through N_1 gives good results, adding the ground states from channels $N_1 + 1$ to N_2 actually worsens the agreement with experiment, while retaining only channels 1 through N_1 but including excited states in these channels brings improved agreement. Or, we may find that keeping ground states leads to real eigenvalues only, while the addition of excited states leads to both real and complex eigenvalues. The latter must be rejected on the grounds given in Sec. II B 4, below Eq. (21).

2. *Future applications*

The preceding calculations are sufficiently accurate for us to believe that the general theoretical methods advocated in this paper can have wide applicability in nonrelativistic quantum mechanics. Two broad areas of interest are immediately evident: molecular physics and nuclear physics, although the implication of the preceding section is that the reduction of a many-channel labeled-particle problem to a single- (or few-) channel problem when identical particles are involved may make the method useful in atomic physics also.

It is of particular importance to note that the strength of the general method lies in its ability to predict *observables* such as R_{eq} and $E^+(R_{eq})$ for the $H_2^+(E<0)$ case, or phase shifts and scattering lengths for $e^- + \mathrm{H}$ scattering,[20,25] and not necessarily to give better wave functions than would be (or are) obtained from more traditional calculations involving the Schrödinger equation. Indeed, in the H_2^+ case, the same approximation to $|\Psi\rangle$ is obtained from all the calculations discussed in the preceding subsections. The basic point is that by writing $|\Psi\rangle$ as a sum over channel components, with their concomitant non-Hermitian matrix (channel) equations, rather than simply expressing $|\Psi\rangle$ as a sum of nonorthogonal basis functions (the two-center functions for the H_2^+ case), one then has a new dynamical procedure for calculating which emphasizes throughout the channel structure inherent in many-body systems.

Naturally, for those cases where extremely accurate numerical calculations have been or can be done, we do not claim that the present method will lead to even better results. Rather, the channel-component method seems best suited for those systems where, because of the complex structure, highly accurate numerical calculations cannot be performed. These include many nonrelativistic quantum systems. It will be interesting to discover if the channel-component method will continue to yield reasonably accurate results. So far, the results are extremely encouraging, particularly as indicated by recent calculations on the H_2 molecule.[30]

ACKNOWLEDGMENT

One of us (FSL) thanks Professor J. Flores and Professor M. Bauer for their hospitality at the Instituto de Fisica, Universidad Nacional Autonoma de Mexico, where most of the first draft of this paper was written.

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*Work supported in part by the United States Energy Research and Development Administration.

†Work supported in part by the Deutsche Forschungsgemeinschaft.

[1] A summary of recent work with references to some of the literature is given in W. Sandhas, Dynamical Equations and Approximation Methods, invited paper presented at the VIIth International Conference on Few-Body Problems, Delhi, India, December 29, 1975–January 4, 1976 (to be published).

[2] A discussion of this for arbitrary n can be found in P. Benoist-Gueutal, Phys. Lett. B 56, 413 (1975).

[3] For example, papers presented at the Second International Conference on Clustering Phenomena in Nuclei, Univ. of Maryland, April, 1975.

[4] F. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968).

[5] The channel-coupling array W was introduced by M. Baer and D. J. Kouri, J. Math. Phys. 14, 1637 (1973). The general many-body scattering theory based on it has been developed, e.g., in D. J. Kouri and F. S. Levin, Bull. Am. Phys. Soc. 19, 489 (1974); Phys. Letts. B 50, 421 (1974); Phys. Rev. A 10, 1616 (1974); Nucl. Phys. A 250, 127 (1975); 253, 395 (1975); W. Tobocman, Phys. Rev. C 9, 2466 (1974); 10, 60 (1974); 11, 43 (1975); 12, 741, 1146 (1975). See also Ref. 7.

[6] Y. Hahn, D. J. Kouri, and F. S. Levin, Phys. Rev. C 10, 1620 (1974).

[7] D. J. Kouri, H. Krüger, and F. S. Levin, Phys. Rev. D (to be published), referred to as I.

[8] F. S. Levin (unpublished); M. L'Huillier (unpublished) (private communication from E. F. Redish). References to the literature on the Bencze-Redish equations are given in Gy. Bencze and E. F. Redish, Nucl. Phys. A 238, 240 (1975).

[9] This is generalization for arbitrary n of the behavior of the Faddeev components[10] for $n=3$, as noted in Ref. 7.

[10] L. D. Faddeev, *Mathematical Aspects of the Three-Body Problem in Quantum Scattering Theory* (Davey and Co., New York, 1965); Sov. Phys.-JETP 12, 1014 (1961).

[11] See Ref. 2.

[12] W. Glöckle, Nucl. Phys. A 158, 257 (1970).

[13] H. Krüger and F.S. Levin, Phys. Lett. 65B, 109 (1976).

[14] We use the word "similar" here, since an approximation may lead to an altered Hamiltonian.

[15] For example, G. Baym, *Lectures on Quantum Mechanics*, (Benjamin, Reading, Mass. 1976).

[16] Ultimately, we must have $\lambda=1$ in order that $\sum_m W_{lm}=1$.

[17] For example, N. Austern, *Direct Nuclear Reaction Theory* (Wiley, New York, 1970); F. S. Levin and H. Feshbach, *Reaction Dynamics* (Gordon and Breach, New York, 1973); J. B. Furness and I. E. McCarthy, J. Phys. B 6, 2280 (1973); 7, 541 (1974).

[18] R. Goldflam and D. J. Kouri, Chem. Phys. Lett. 34, 594 (1975). The possible use of Eq. (7) for molecular-bound-state calculations has also been noted in this work.

[19] B. L. Moiseiwitsch, *Variational Principles* (Wiley, New York, 1966).

[20] D. J. Kouri, F. S. Levin, M. Craigie, and D. Secrest, J. Chem. Phys. (to be published); D. J. Kouri and F. S. Levin, Proceedings of the Quebec Conference, 1974, in *Few-Body Problems in Nuclear and Particle Physics*, edited by R. J. Slobodrian, B. Cujec, and K. Ramavataram. (Laval U. P., Quebec, 1975), p. 47.

[21] The bound-state approximation can be used with the Faddeev-Lovelace choice of W (see Refs. 5 or 7), at least when $n=3$, as noted in I.

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[26] H. Krüger (unpublished calculations).

[27] F. S. Levin, Application of the Channel Coupling Array Method to Atomic Few-Body Systems, invited paper presented at the VIIth International Conference on Few-

Body Problems, Delhi, India, December 29, 1975,–January 4, 1976 (to be published in the Proceedings). A sketch of the H_2^+ results was first given in this paper, and a slightly more detailed account can be found in H. Krüger and F.S. Levin, Chem. Phys. Lett. (to be published).

[28] See, e.g., W. Orville-Thomas, *The Structure of Small Molecules* (Elsevier, New York, 1966).

[29] D. J. Kouri, F. S. Levin, M. Craigie, and D. Secrest, J. Chem. Phys. 61, 17 (1974) and in press; D. J. Kouri and F. S. Levin, Phys. Rev. C 13, 14 (1976).

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