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Channel-coupling theory of covalent bonding in H_2: A further application of arrangement-channel quantum mechanics

F. S. Levin*
Physics Department, Brown University, Providence, Rhode Island 02912

H. Krüger†
Fachbereich Physik, Universitat Kaiserslautern, Kaiserslautern, Germany

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The dissociation energy D_e and the equilibrium proton-proton separation R_{eq} of H_2 are calculated using the methods of arrangement-channel quantum mechanics. This theory is the channel component version of the channel-coupling array approach to many-body scattering, applied to bound-state problems. In the approximation used herein, the wave function is identical to that of the classic Heitler-London-Sugiura valence-bond calculation, which gave $D_e = 3.14$ eV and $R_{eq} = 1.65a_0$, values accurate to 34% and 17.8%, respectively. The present method yields $D_e = 4.437$ eV and $R_{eq} \simeq 1.42a_0$, accurate to 6.5% and 1%, respectively. Some implications of these results are discussed.

I. PROCEDURE AND RESULTS

We have previously described[1] a new method for bound-state calculations and applied it to the H_2^+ molecular ion. This method is based on the channel-coupling array theory of multichannel scattering.[2] Here, we present results for the H_2 ground state, also based on the theory of II. As we show, the values of R_{eq}, the proton-proton equilibrium separation, and D_e, the dissociation energy into two ground-state hydrogen atoms, are more accurate than their corresponding values[1] for H_2^+, even though correspondingly crude wave functions are used and the present system is more complicated, being a four- rather than a three-body molecule. The implications of this are discussed below.

The form of the channel-coupling array theory used is denoted arrangement-channel quantum mechanics.[1,3] The channels correspond to different partitions into bound clusters of the particles forming the system (distinguishability of particles is initially assumed; particle identity is introduced by taking appropriate linear combinations of distinguishable particle wave functions or amplitudes). In this theory, the Schrödinger wave function Ψ is expanded into channel components[1,3] ψ_j corresponding to the various channels (denoted j):

$$\Psi = \sum_j \psi_j . \tag{1}$$

In order that (1) be exact, the sum on j should run over at least all two-body channels[1,4] [i.e., channels in which there are only two bound clusters of (distinguishable) particles].

Equation (1) is an "expansion" into nonorthogonal states ψ_j: $\langle\psi_j|\psi_k\rangle \neq 0$, $k \neq j$. The ψ_j are defined[1-3] by the set of equations

$$(E - H_j)\psi_j = \sum_k W_{jk} V_k \psi_k, \quad \text{all } j, \tag{2}$$

plus appropriate boundary conditions ($E<0$ or $E \geq 0$). The notation of (2) is as follows. E is the energy; W_{jk} is an element of the (real) channel coupling array W satisfying $\sum_j W_{jk} = 1$, examples of which can be found in Refs. 2; and H_j and V_j are the channel Hamiltonian and channel interaction in channel j, such that V_j is the intercluster interaction, which goes to zero as all intercluster separations become asymptotic. H_j contains the kinetic energies and the intracluster binding interactions, and is related to the Schrödinger Hamiltonian H by $H_j = H - V_j$. We note that Eq. (2) is *exact*, and if both sides of it are summed on j, can easily be seen to lead via (1) and the normalization condition $\sum_j W_{jk} = 1$ to the Schrödinger equation $(E - H)\Psi = 0$. Equations (1) and (2) are the basic equations of theory. We now apply them to the H_2 molecule.

H_2 is made up of two protons, labeled A and B, and two electrons, labeled 1 and 2. For positive energies, H_2 can exist (asymptotically) in six different two-body channels as follows:

$$\left.\begin{array}{ll}\text{channel (1):} & (A,1)+(B,2)\\ \text{channel (2):} & (A,2)+(B,1)\end{array}\right\} \mathrm{H}+\mathrm{H},$$

$$\left.\begin{array}{ll}\text{channel (3):} & (A,12)+B\\ \text{channel (4):} & A+(B,12)\end{array}\right\} \mathrm{H}^-+\mathrm{H}^+,$$

$$\left.\begin{array}{ll}\text{channel (5):} & (AB,1)+2\\ \text{channel (6):} & (AB,2)+1\end{array}\right\} \mathrm{H}_2^+ + e^- .$$

We use the notation (nucleus, electrons) to denote a bound cluster of particles and "+" to mean noninteracting. The calculations we report on here are based on a two-channel approximation in which we retain only channels (1) and (2) above. Schematic diagrams of the coordinates used in our analysis of H_2 and the partitions forming channels 1 and 2 are shown in Fig. 1.

In the Born-Oppenheimer approximation,[5] the Schrödinger Hamiltonian H is

$$H = K - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}, \tag{3}$$

where K is the sum of the electron kinetic energies, r_{Aj} and r_{Bj} are relative separations of electron j from protons A and B, r_{12} is the interelectronic separation, and R is the usual proton-proton separation[5] (Fig. 1). The partitionings of H into $H_j + V_j$ for the two channels we retain in the calculation are (Fig. 1)

$$H_1 = K - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B2}}, \quad V_1 = -\frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} + \frac{e^2}{r_{12}} + \frac{e^2}{R} \tag{4a}$$

and

$$H_2 = K - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}}, \quad V_2 = -\frac{e^2}{r_{A1}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}. \tag{4b}$$

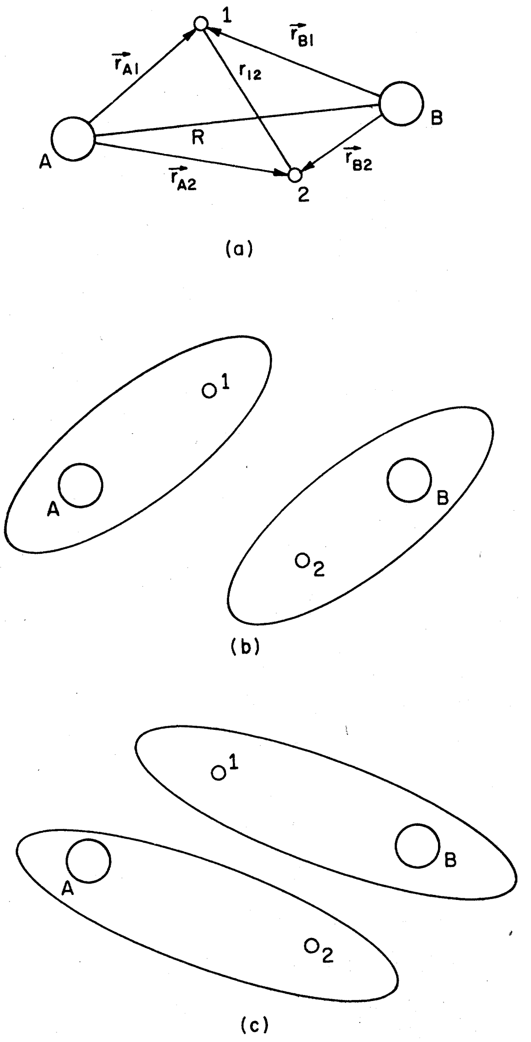

FIG. 1. Schematic diagrams of the H_2 molecule: (a) coordinates; (b) bound clusters (labeled H atoms) forming channel 1; (c) bound clusters (labeled H atoms) forming channel 2.

The channel-coupling array W appropriate for a two-channel problem is[1,2,6]

$$W = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{5}$$

Use of (5) in (2) yields[7]

$$(E - H_1)\psi_1 = V_2\psi_2, \tag{6a}$$

$$(E - H_2)\psi_2 = V_1\psi_1, \tag{6b}$$

where from (1), $\Psi = \psi_1 + \psi_2$.

Comparison of Eqs. (6a) and (6b) with those of Ref. 1 for H_2^+ show that they are the same pair in each case; only the detailed structure of the H_i and V_i will change as we go from H_2^+ to H_2 (or[8] to H^-, He, Li^+, etc.). Notice, however, that this is the pair for a *two-channel*, not a *two-particle* system.

We may obtain approximate solutions to (6) by using the projection-diagonalization method of Ref. 1. In this method, each ψ_j, H_j, and V_j is projected onto a subspace spanned by a limited number of states defined for each channel j. In accordance with the $E > 0$ result proved in Ref. 3 that ψ_j asymptotically is the full Ψ in (two body) channel j, these states are chosen from the bound-cluster eigenstates of the H_j, although one could of course include continuum states (as would be necessary in an exact expansion of ψ_j). In the present case, this means using one or more products of the form $\eta_\alpha(\vec{r}_{Aj})\eta_\beta(\vec{r}_{Bk})$, $j=1$, $k=2$, or $j=2$, $k=1$, where η_α is the αth($\alpha = nlm$) state of hydrogen. In our calculations we have retained only the ground state, $\alpha = 1s$, for each atom:

$$\psi_1 = a_1(R)\eta_{1s}(r_{A1})\eta_{1s}(r_{B2}), \tag{7a}$$

$$\psi_2 = a_2(R)\eta_{1s}(r_{A2})\eta_{1s}(r_{B1}), \tag{7b}$$

where $a_j(R)$ is to be determined.

According to the theory given in Ref. 1, the a_j and E are determined from a secular equation obtained by substitution of (7) in (6) followed by projection of both sides of (6a) onto $a_1^{-1}\psi_1$ and of (6b) onto $a_2^{-1}\psi_2$:

$$\begin{pmatrix} \epsilon_0 - E & M(R) \\ M(R) & \epsilon_0 - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0, \tag{8}$$

where $\epsilon_0 = -e^2/a_0$, and $M(R)$ is either of two matrix elements, e.g.,

$$M(R)=\epsilon_0\langle\eta_{1s}(r_{A1})\eta_{1s}(r_{B2})\,|\,[(1/r_{A1}+1/r_{B2}-1/r_{12}-1/R)\,|\,\eta_{1s}(r_{B1})\eta_{1s}(r_{A2})\rangle\,, \tag{9}$$

with all lengths in units of the Bohr radius a_0. We point out that, while an alternative equation can be obtained by projecting (6a) onto $a_2^{-1}\psi_2$ and (6b) onto $a_1^{-1}\psi_1$, the fact that we are working with the negative energy continuation of an $E>0$ theory means that (8) is the proper form.[1]

This latter point is extremely important, since inspection of the pair (6) plus the ansatz (7) does not imply a unique way to proceed. Indeed, addition of the alternative equation noted in the preceding paragraph [below Eq. (9)] to (8) would lead to the *variational* equation as an approximation to the Schrödinger equation, obtained by use in the Rayleigh-Ritz variational principle[5] of $\Psi=\psi_1+\psi_2$ as a trial function, with variational parameters a_1 and a_2 from the ψ_1 and ψ_2 defined by (7). However, as stressed in II, one must project in the manner stated above Eq. (8), in accord with the present approach being the negative energy continuation of an $E>0$, many-body scattering theory. For, when $E>0$, the projection in channel j is onto the bound states of the bound clusters forming channel j, i.e., onto the bound states of that portion of H_j describing the internal states of the bound clusters. In the present case, this means (6a) is to be projected onto states of $(K_1-e^2/r_{A1})+(K_2-e^2/r_{B2})$, while (6b) is to be projected onto states of $(K_1-e^2/r_{B1})+(K_2-e^2/r_{A2})$. The states to be used, respectively, are those occurring in (7a) and (7b), that is, $a_1^{-1}\psi_1$ and $a_2^{-1}\psi_2$, as stated above Eq. (8).

Equation (8) yields two solutions for E given by

$$E^{\pm}(R)=\epsilon_0\pm M(R), \tag{10}$$

corresponding to bonding (+) and nonbonding (−) orbitals. We consider only the former case here. The dissociation energy D_e is given by $-M(R_{eq})$, where R_{eq} is the value at which E^+ is a minimum. The four terms in (9) are well-known quantities in molecular quantum mechanics and have each been evaluated analytically.[5,9] We show in Fig. 2 plots of $E^+(R)-\epsilon_0$, comparing the present results with those of Kolos and Roothaan who used a 40-term variational wave function[10] and also with those resulting from use of the simple Heitler-London valence-bond variational wave function.[11]

The variational method, and in particular the Heitler-London calculation, is of sufficient interest for our purposes that we briefly review it here (see Ref. 5 for details). For a trial function one uses

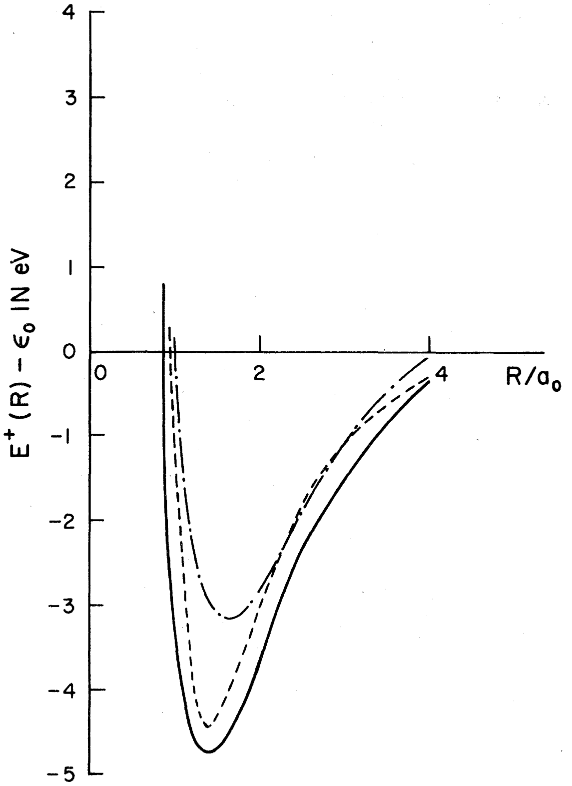

FIG. 2. Comparisons of $E^+(R)-\epsilon_0$ for (a) the Kolos-Roothaan calculation (solid line); (b) the Heitler-London calculation (dot-dashed line); and (c) the present, arrangement-channel calculation (dashed line).

$$\Psi_t^{H\text{-}L}=a_1'\eta_{1s}(r_{A1})\eta_{1s}(r_{B1})+a_2'\eta_{1s}(r_{A2})\eta_{1s}(r_{B1})\,, \tag{11}$$

with a_1' and a_2' being the variational parameters of interest. Evaluation of

$$E_t=\langle\Psi_t^{H\text{-}L}|H|\Psi_t^{H\text{-}L}\rangle/\langle\Psi_t^{H\text{-}L}|\Psi_t^{H\text{-}L}\rangle,$$

with H given by Eq. (3), leads to an upper bound for the energy. It is found that E_t is given by[5]

$$E_t^{\pm}=\epsilon_0+(Q\pm A)/(1\pm\Delta^2)\,, \tag{12}$$

where[5]

$$Q=\epsilon_0\langle\eta_{1s}(r_{A1})\eta_{1s}(r_{B2})\,|\,(1/r_{A1}+1/r_{B2}-1/r_{12}-1/R)\,|\,\eta_{1s}(r_{A1})\eta_{1s}(r_{B2})\rangle\,, \tag{13}$$

$$A\equiv M(R), \tag{14}$$

and

$$\Delta(R)=\langle\eta_{1s}(r_{Aj})\,|\,\eta_{1s}(r_{Bj})\rangle=(1+R+\tfrac{1}{3}R^2)e^{-R},\quad j=1,2.$$

Since $M(R)$ is given by Eq. (9) we see that Q and A correspond, in the language of arrangement-channel quantum mechanics, to direct and exchange matrix elements of (either of) the channel interactions. We postpone a comparison of the expressions (10) and (12) for the energy until below, but we note here that[5] $a_1' = \pm a_2' = (1 \pm \Delta^2)^{-1}$, and also that the a_i of Eq. (7) are equal to a_i': $a_i = a_i'$. Hence, just as was found[1] for H_2^+, the approximate Ψ obtained from the channel-coupling calculation is *identical* to the wave function found from the simple variational approach, in this case $\Psi_t^{H\text{-}L}$, even though the two approximation methods, viz. the diagonalization approach of arrangement-channel quantum mechanics and the Rayleigh-Ritz variational method, lead to different energies.[1] We also comment on this below.

The values of R_{eq}, $D_e = \epsilon_0 - E(R_{eq})$, and $E(R_{eq})$ for the bonding case are given in Table I for the nonrelativistically "exact" calculation of Kolos and Roothaan (which agrees with the experimental results of Stoicheff[12] as quoted by Pilar[5]), for the Heitler-London valence-bond calculation, and for the present, arrangement-channel case. The accuracy of R_{eq} and D_e for the valence-bond calculation is not good, as is well-known, being 82 and 66%, respectively. On the other hand, for the arrangement channel case, R_{eq} and D_e are 99 and 93.5% accurate, respectively. Clearly the dynamical procedure in this latter case is superior to that of the standard Rayleigh-Ritz variational approach, since the resulting approximate wave function is the same in the two methods. Indeed this must be the case, because the variational procedure leads to a dissociation energy containing no effects of correlation, while the arrangement-channel calculation yields a value of D_e containing 72% of the correlation energy[13] of 1.11 eV, even though $\Psi = \psi_1 + \psi_2$ for the bonding (spin singlet) case contains Pauli principle correlations but no in-out, left-right, or angular correlations.[5] Also, the approximate arrangement-channel wave function has the correct dissociation behavior.

The valence-bond wave function is, of course, not the only relatively simple variational wave function used for H_2 calculations. While its D_e is more accurate than that from a molecular-orbital calculation,[5] it would seem that almost all other trial functions have led to values of D_e and R_{eq} more accurate than those of the valence-bond approach, as, e.g., the tabulation of McLean, Weiss, and Yoshimine[14] shows. Nevertheless, of the more than 50 sets of variational results listed by these latter authors, only four, apart from calculations of Kolos and collaborators, yield values of D_e more accurate than obtained from the combination of Heitler-London valence-bond wave function and diagonalization procedure of this paper. The less accurate results include those based on scaled wave functions, correlated wave functions, and multiparameter, single-center wave functions. Thus, for H_2, not only is the simple arrangement-channel calculation more accurate than the valence-bond computation, it is also more accurate than most of the reported variational calculations, unless these calculations employ (apparently) very accurate trial wave functions.

TABLE I. Comparison of H_2 ground-state observables.

	R_{eq}/a_0	$E^+(R_{eq})$ (eV)	D_e (eV)
Exact[a]	1.40	−31.956	4.746
Heitler-London[b]	1.65	−30.35	3.14
Arrangement channel	1.42	−31.647	4.437

[a] References 10 and 12.

[b] Reference 5.

II. IMPLICATIONS

The preceding analysis and remarks suggest several conclusions:

(i) *In terms of obtaining relatively high accuracy using relatively simple input, the arrangement-channel method is, thus far, superior to the Rayleigh-Ritz variational approach for ground-state calculations*. This is achieved not by using an approximate function constrained as in the variational approach,[15] but by effectively altering the Schrödinger equation itself. Relatively accurate results are achieved by applying a new dynamical procedure in which the channel nature of a many-body system is emphasized,[1] and not by seeking an unusual wave function to be used in a traditional calculation. This raises some questions to be sure (see below), but also allows one to gain some insight into the dynamics of the system. We do this by comparing the two expressions for the energy, Eqs. (10) and (12), in the case of bonding. It is clear from the discussions of H_2 given by Pilar[5] or Slater,[9] that no special significance can be ascribed to the structure of (12): the physical picture of bonding arising from the Heitler-London approach is a result of the structure of the trial function (11) and its use in determining the kinetic and potential energies of the system.[5,9,16] There seems, in the H_2 case, to be no special role played by the valence-bond Coulombic and exchange integrals Q and A. A very different situation is obtained in the case of Eq. (10), for $M(R)$ is the key to understanding bonding in the arrangement-channel approach. As noted in II (see also below), the channel components ψ_1 and ψ_2, when combined to form Ψ, lead to symmetric or antisymmetric states: effects of the Pauli principle are treated by particular combinations of labeled-particle quantities, and thus enter the results by means of matrix elements taken between states in different channels. $M(R)$ is just such a matrix element. If $M(R)$ is set equal to zero (no channel interactions), then the approximate energy is just the sum of the energies of the two ground-state H atoms; the value is the same no matter which channel is considered, and the system is essentially in a state in which $R=\infty$, i.e., in its asymptotic channel states. By evaluating $M(R)$, we allow the two channels to interact and form the (possibly) bound H_2 system. If $M(R)<0$, the system will be bound. Binding results if the magnitude of the channel-averaged (electron-proton) attraction in either channel is greater than the magnitude of the channel-averaged (electron-electron and proton-proton) repulsion.[1] Obviously bonding occurs, and, for example, we find that at R_{eq}, the channel-averaged attraction is -24.775 eV while the repulsion is 20.338 eV. $M(R)$ articulates this interplay in what we believe is a particularly simple way.

(ii) *The results of this paper for R_{eq} and D_e seem accurate enough, unlike those of the Heitler-London procedure, to validate the classic picture of covalent bonding in H_2: two ground-state H atoms sharing electrons.* Although this physical picture is suggested by the Heitler-London results, these results are not accurate enough to use $\Psi_t^{H\text{-}L}$ and the variational procedure as a model for H_2. As refinements are made in the trial wave function,[5,14] the accuracy of R_{eq} and D_e and thus the model of H_2 improves, but the physical picture, and consequently our understanding of the bonding mechanism, deteriorates. The ultimate and not unexpected conclusion is that the most accurate variational calculations of R_{eq} and D_e give essentially perfect agreement with experiment,[12] but fail to provide a physical picture from which any simple bonding model can be constructed.[5] This lack of a simple model which produces relatively accurate results has long been an unsolved problem in the quantum theory of chemical bonding. By use of arrangement-channel quantum mechanics we have provided a solution to this problem by demonstrating the existence of a new calculational technique which, when coupled with the old valence-bond wave function, yields a model whose results are sufficiently accurate as to validate the classic picture of the covalent bond.

(iii) *The present result, along with that for H_2^+, strongly supports our previous expectation[1] that arrangement-channel quantum mechanics could be a useful technique for solving bound-state problems, that is, the results for H_2^+ are not fortuitous* (as the He atom calculations also indicate[8]). What is most interesting in comparing our H_2 and H_2^+ results is that use of equally crude approximations in each case has lead to more accurate values of R_{eq} and D_e for H_2, the more complicated system. The implication, which we endorse, is that H_2 is better approximated as a pair of ground-state H atoms (subject to the Pauli principle) than is H_2^+ by its one electron being in an H-atom ground state. This is easily understood classically, despite R_{eq} being smaller for H_2 than H_2^+. The point is that in H_2^+, the proton not forming the H atom will, because of its net nonzero charge, polarize the H atom much more easily than either of the (neutral) H atoms will polarize the other one in the H_2 system. Hence, H_2^+ should have considerably more nonspherical components than should H_2, and this is reflected in the calculated H_2^+ energy being less accurate than that of H_2 in the simple arrangement-channel calculations reported so far. A possible, further implication is that in larger neutral molecules, use of the ground states of the constituent atoms may be as accurate an approximation to the molecular wave function as we have found for H_2.

(iv) *The preceding three conclusions suggest a fourth: arrangement-channel quantum mechanics may provide a framework that can validate the "atoms-in-molecules" method of Moffitt*,[17,18] which has not been as successful as Moffitt had anticipated.[5] Such a validation would occur if, on using the ground states of the constituent atoms in a molecule as the channel states, with their concomitant ground-state energies playing a role analogous to ϵ_0 of Eqs. (8) and (10), the calculation of the quantity analogous to $M(R)$ of Eqs. (8)–(10) would lead to a value of D_e for the molecule whose accuracy would be comparable to that obtained in the present case for H_2. Certainly, one can say that the atoms-in-molecules method does work for H_2 when we use the framework of arrangement-channel quantum mechanics.

In addition to suggesting the preceding conclusions, our work raises a number of questions:

(i) Accepting the above conclusions, particularly (ii) at face value, what then is the meaning of the approximate Ψ? Or alternatively, as in the second of Ref. 1, according to the present method, how is the electron density distribution to be determined? The answers are essentially the same: the approximation to the exact wave function is precisely the Ψ as given above, i.e., (bonding case),

$$\Psi^+(1,2)=[2(1+\Delta^2)]^{-1/2}[\eta_{1s}(r_{A1})\eta_{1s}(r_{B2})+\eta_{1s}(r_{B1})\eta_{1s}(r_{A2})]\,, \qquad (15)$$

and this Ψ^+ is to be used to determine the electronic density $\rho^+(r_1)$ by

$$\rho^+(r_1) = \int d^3r_2 \, |\Psi^+(r_1, r_2)|^2 \, . \tag{16}$$

There are two comments relevant to this. First, as stressed in II, one should not use an approximate wave function without bearing in mind (and stating when necessary) both the dynamical procedure from which the approximation has been derived and also those dynamical properties it predicts well and those it predicts poorly. This is as true for the variational method as it is for the present approach. Second, use of the same approximate wave function with two different dynamical procedures yielding at least one different dynamical property means that there are actually two (rather than one) approximate wave functions. That is (again), one really must couple together the wave function and the dynamical method which employs it. For example, Eq. (15) is a relatively accurate wave function in an arrangement-channel sense, since to produce the *same* R_{eq} and D_e (assuming this to be possible) from the variational method would require a much more complicated trial function[12] than (15). As suggested by Johnson,[19] one might construct such a trial function, say $\tilde{\Psi}_t$, by solving

$$[\epsilon_0 + M(R) - H]\tilde{\Psi}_t = 0 \tag{17}$$

in some fashion, perhaps by expansion in a suitable set of functions or even self-consistently.

(ii) Given that channels are defined by partitionings among labeled particles, and that electrons are identical particles, how are the proper symmetry conditions on the overall space-spin wave function to be introduced? In the present case of a spin-independent Hamiltonian and identical fermions, this is done by using spin-wave functions whose symmetry under particle interchange is opposite to that of the space wave function. Notice that this implies $\psi_2 = \pm P_{21}\psi_1$, where P_{21} is the two-particle transposition operator. In the general case, initially more complicated procedures must be followed, but they ultimately lead to a reduction in the number of equations to be solved, as noted in II. This reduction is one of the advantages inherent in using the present theory. In particular, the pair (6) can be reduced to a single equation which will give the same numerical results as (8), i.e., Eq. (10). This reduction in the two-channel case is discussed in II for the H_2^+ problem. In all cases, however, one has *a priori* knowledge of the symmetry properties, and these are to be imposed as part of the solution of the problem. This is trivial to do in a two-channel approximation as in the present case, where +(−) uniquely corresponds to spin singlet [triplet, but see iv(a) below].

(iii) Given that in the Heitler-London variational procedure E_t^- corresponds to the lowest *anti*bonding (spin triplet) state, what is the meaning of the *non*bonding value E^- in the arrangement-channel case? The answer is that in terms of the present approximation, E^- is without meaning, i.e., it is a spurious[20] solution and should be disregarded. That is, $\epsilon_0 - M(R) = E^-(R)$ has the wrong behavior as $R \to 0$ (it implies infinitely strong binding) and thus is an unacceptable energy "surface" on physical grounds. This mimics the similar behavior of the nonbonding solution for H_2^+ (see II), and is a shortcoming, so far, of arrangement-channel calculations that use one channel state in the basis expansions of the ψ_j. In the case of H_2^+ we know[21] that use of excited basis states in the expansion of the ψ_j eliminates this problem, and we may expect a similar result in the case of H_2. This leads us immediately to the next question, viz. the role of excited H-atom states and the rate of convergence of an H-atom basis expansion.

(iv) Since the four conclusions reached above are based on a calculation involving only the ground states in the two channels, the obvious, and perhaps the most important, questions raised by our work are: how fast does an expansion using excited hydrogenic states converge, and what role is played by the four channels neglected in the present work? These questions are obviously linked, since it may turn out that convergence could be achieved only by inclusion of other channels. Although the first of these two questions is the subject of current investigation, some work has been done which bears on the second, and it is also possible to comment on convergence rates in other calculations.

(a) Two sets of calculations involving channels (3) and (4) have been caried out. These have involved two different approximations to the H^- wave function, the first being a symmetrized product of H-atom ground states, as in conventional procedures involving "ionic" contributions[5] to H_2, and the other being the Chandrasekhar variational function[22] $\Psi_t^C = N[e^{-ar_1}e^{-br_2} + 1 \leftrightarrow 2]$, where r_1 and r_2 are electron coordinates relative to a fixed center, $a = 1.039$, and $b = 0.283$. Use of these two approximations leads to very different results. The first one yields $R_{eq} \cong 1.10a_0$, and $E^+(R_{eq}) = -28.88$ eV, thus inadequately approximating both MO[5] and the preceding results. The more realistic Ψ_t^C yields an excited state with $R_{eq} = 2.15a_0$, and $E^+(R_{eq}) = -16.69$ eV, where it has been assumed that Ψ_t^C is exact, giving the H^- affinity rather than approximately 50% of its value as found by Chandrasekhar.[22] This of course will make only a small change in the value −16.69 eV, and we believe that this value is a reasonable approximation to an excited H_2 singlet state embedded in the H + H continuum. For precisely the same reason as in question (iii) preceding, no meaningful triplet states occur. We have also carried out four-channel calculations, based on channels (1)–(4), using the sets of wave functions just described. Without imposing the requirement of antisymmetry, but simply solving the 4×4 secular equation, we find no solutions corresponding to singlet or triplet spins: the spatial wave functions in all cases are of mixed symmetry and are also spurious.[20] Further calculations in which the symmetry condition is imposed from the beginning are currently being investigated and will be discussed subsequently as part of a larger analysis of convergence and excited H_2 states.

(b) While no results on inclusion of excited H-atom states in the expansion of the ψ_j are yet available for H_2, some information is available from the H_2^+ calculations[21] and the He-atom calculations.[8] In the former case, it is found[21] that inclusion of the $2s$ or $2p_0$ state yields an antibonding (σ_u state) without substantially altering the singlet ground-state result. Addition of $2p_x$ and $2p_y$ again leaves the ground state essentially unchanged, but introduces a conjugate pair of complex energy eigenvalues whose possible existence has been noted in I and II (see also Ref. 20). Inclusion of $n = 3$ states for this system will be undertaken in the future. Calculations for the ground state $E(gs)$ of He have included hydrogenic $1s$, $2s$, and $3s$ states for $Z = 2$. Retaining only $1s$ gives $E(gs)$ accurate to 5%, while addition of the $2s$ and $3s$ states improves the accuracy by an order of magnitude. While no conclusions regarding the H_2 system can be drawn from these results, they are encouraging. The reason is as follows. Use of $1s$ through $3s$ states in the He calculations give approximations for $E(gs)$ which lie above the exact value and which converge rapidly towards it. The crudest H_2^+ calculation leads to an approximate $E(gs)$ lying *below* the exact value, and all improvements so far have led to values of $E(gs)$ that remain below the exact value. However, the H_2 calculation, unlike that for H_2^+, gives an approximation to $E(gs)$ which also lies *above* the exact value. Hence, a calculation for H_2 using both $1s$ and $2s$ states which would lead to improved accuracy and a value lying above the exact one would not be unexpected.

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