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Channel-coupling theory of molecular structure. Global basis-set expansions for $H_2{}^+$, H_2, and HeH^+

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Earlier work applying equations of the channel-coupling array theory of many-body scattering to $H_2{}^+$ and H_2 has been extended. Primary consideration has been given to the use of the Galerkin-Petrov method, by which the non-Hermitian matrix equations of the theory have been solved approximately with the use of globally defined bases as expansion sets. For $H_2{}^+$, both hydrogenic and Hylleraas-Shull-Löwdin functions were used, but neither set led to minima in the ground-state *(gerade)* potential-energy curves which lie higher than the exact value nor indicated a convergence to the correct minimum value. Only hydrogenic functions were used for H_2 in a two-channel truncation approximation. Slow convergence (from above) to the exact minimum in the singlet ground-state potential-energy curve was indicated. The inner minimum in the H_2 $E\,{}^1\Sigma_g^+$ curve originally calculated by Davidson was reproduced to within 0.002 a.u. by an extremely simple covalent approximate calculation; there was no indication of Davidson's outer, ionic minimum, but this is not surprising since an ionic component was not built into our approximation. The HeH^+ ground state was also determined. The equilibrium separation and energy minimum for the ground state was relatively accurate given the simple (Eckart) wave function used to approximate the He ground state. In addition to these results, the nonphysical $H_2{}^+$ *ungerade* and H_2 triplet potential-energy curves found in the earlier one-state approximate calculations also occurred in the present computations. The failure to achieve accurate convergence and the persistence of nonphysical potential-energy curves remain serious problems that require further investigation. A resolution of both these problems for $H_2{}^+$ has been achieved and is described in the following paper.

I. INTRODUCTION

Collisions involving few-body systems occur in many branches of physics, well-known examples being low-energy neutron-deuteron or atom-diatom scattering. These are among the simplest realistic examples in which the total number n of interacting constituents is greater than 2. It is by now well established that in order to describe n-particle collisions rigorously when $n>2$ one must use one or another form of many-body scattering theory,[1] and not simply the Schrödinger equation supplemented by a single Lippmann-Schwinger equation to express the boundary conditions, as in the case[2] $n=1$ or 2. Many-body scattering theories have been applied not only to various nuclear, atomic, and molecular collision problems, but also to the calculation of bound states. Early work in this latter direction using one form or another of Faddeev[3] or Alt, Grassberger, and Sandhas[4] (AGS) equations examined bound states of strongly interacting systems of bosons or fermions[5] and also of systems of three charged particles.[6] One of the characteristic results arising in the latter applications, as studied in great detail by Chen and collaborators,[6] is a slow and nonmonotonic convergence toward the exact results. One effect of this has been an understandable lack of continued interest in studying bound states of three charged particles via Faddeev-type equations, particularly because convergence can only be achieved if one uses, for example, the entire (infinite) set of bound and continuum hydrogenic states or the infinite set of Sturmian functions as separable expansion bases.[6]

More recently, an alternate set of many-body scattering equations has been applied to bound-state problems. This is the set of channel-coupling array (CCA) equations obtained with a channel-permuting array (CPA), which we shall refer to simply as the CPA equations.[7] In contrast to the Faddeev or equivalent AGS three-body equations, the CPA equations are not limited to the case $n=3$. As a result, they have been previously applied not only to bound states of certain three-charged-particle systems, viz., the hydrogen molecular ion[8] ($H_2{}^+$) (hereafter, paper I) and some two-electron atoms[9] (H^-, He, Li^+), but also to the structure of the hydrogen molecule[10] (H_2), a four-particle system.

The procedure followed in all these bound-state applications was to solve the various many-body scattering equations as an eigenvalue problem. In effect, this has meant attempting to determine the poles and residues of the many-body transition operators. This has usually been done by solving approximately the homogeneous equations which define the wave-function components ψ_j of the particular theory.[11] In the case of the CPA equations as applied to $H_2{}^+$ and H_2, a pair of coupled equations for two components ψ_1 and ψ_2 (differing for $H_2{}^+$ and H_2 of course[8,10]) was solved approximately by expanding ψ_1 and ψ_2 each in terms of appropriate hydrogenic functions and then retaining only the first state (1*s*). The salient features of the results are as follows. For $H_2{}^+$, the CPA approximation to the *gerade* Schrödinger wave function Ψ^g (given by $\psi_1+\psi_2$) was the simplest molecular orbital function Ψ^{MO}, while the CPA *gerade* potential-energy curve $E^g_{\text{CPA}}(R)$ was much more accurate than the perturbatively determined one using Ψ^{MO} as a trial function.[8] (Here, R is the usual internuclear separation.) In particular, the CPA equilibrium separation R_e was $2.07a_0$, compared to the perturbation (Ψ^{MO}) result of $2.50a_0$ and the exact result of $2.00a_0$, while the minimum of the *gerade* potential curves were -0.6132, -0.5654, and -0.6026 a.u., respectively. The CPA result lies lower than the exact one, a point discussed below. In contrast, the CPA calculation of the $H_2{}^+$ *ungerade* potential-energy curve $E^u_{\text{CPA}}(R)$ produced an unphysical ("spurious") result since in the limit $R\rightarrow 0$, $E^u_{\text{CPA}}(R)\rightarrow -\infty$. For H_2, the CPA approximation to the singlet Schrödinger wave function Ψ^+ (again given by $\psi_1+\psi_2$) was equal to the Heitler-London valence-bond function Ψ^{VB}, while the CPA singlet potential energy $E^+_{\text{CPA}}(R)$ was again much more accurate than the variationally determined one using Ψ^{VB} as a trial function.[10] In particular, the CPA value of R_e was $1.42a_0$ while the VB and exact values were $1.65a_0$ and $1.40a_0$, and the corresponding values of the minimum in the singlet potential-energy curves were -1.163, -1.115, and -1.1744 a.u., respectively. The preceding CPA value actually contains 72% of the correlation energy.[10] In contrast, the CPA H_2 triplet potential-energy curve $E^-_{\text{CPA}}(R)$ showed the same unphysical behavior as the $H_2{}^+$ *ungerade* curve $E^u_{\text{CPA}}(R)$, viz., in limit $R\rightarrow 0$, $E^-_{\text{CPA}}(R)\rightarrow -\infty$.

These results may be compared with those arising from standard Schrödinger-equation-based variational calculations. The occurrence of approximate energies lying lower than exact ones (see also Ref. 6) and, in the atomic calculations,[9] of a nonmonotonic behavior of the energies with increase in the basis, can be understood as formalism-dependent results, as follows. Both the CPA and the Faddeev wave-function formalisms can be expressed as a Schrödinger-type equation in matrix form, but with the unusual feature that the Hamiltonian-type operator matrix appearing in the equation is non-Hermitian[12]: $\underline{H}^\dagger\neq\underline{H}$. An immediate consequence of this is the nonexistence of a Hylleraas-Undheim theorem[13] for the CPA and Faddeev wave-function formalisms. That is, there is no guarantee that approximate solutions to these non-Hermitian operator equations will either yield bounds on the energies or a monotonic convergence of the computed energies with increase in size of the basis set used in making the approximations. Lack of a Hylleraas-Undheim theorem suggests that the behavior which the existence of theorem would prevent will actually occur; the results noted above verify this.

The occurrence of the unphysical $H_2{}^+$ *ungerade* and H_2 triplet results is consistent with the use of a non-Hermitian CPA formalism. It is known that the CCA theory, like many other n-particle scattering theories (but not the AGS or Faddeev formalisms), can yield spurious solutions.[14] A spuriosity arises when $\sum_j\psi_j=0$, where the j sum is over the partitions or arrangement channels of the n-particle system. In the present instances, $\sum_j\psi_j=0$ occurs for both the $H_2{}^+$ *ungerade* and the H_2 triplet cases, but only in the limit $R\rightarrow 0$. Hence the negative infinity in the approximate *ungerade* and triplet energy curves at $R=0$ is in each case a spuriosity. Nevertheless, for R small but not equal to zero, $\sum_j\psi_j\neq 0$, while the energy values are still negative and attractive rather than positive and thus repulsive, as required on physical grounds. Thus these unphysical potential-energy curves are not true spuriosities. Their meaning and a reason for their occurrence will be discussed in the following paper.[15]

The foregoing results suggest that these first CPA molecular structure calculations, which involve extremely simple approximations and have led to some unexpectedly accurate results, might well be usefully extended. The non-Hermitian CPA formalism as used for bound-state computations needs to be understood better; in particular, questions concerning effects of increasing the expansion set, elimination of unphysical results, and convergence to exact results remain to be answered. In this paper and the following one, we provide answers to the questions just alluded to. Our main purpose has been to investigate convergence by means of increasing the size of the expansion basis. This is done in the present paper by using expansion functions which are defined *globally,* i.e., over all of configuration or momentum space. In addition, we investigate also both a variational method for $H_2{}^+$ using the CPA formalism and the use of approximations to the basis states in the case of HeH^+. Our general conclusion is that use of a limited basis of globally defined functions does not lead to convergence. This raises various questions concerning the formalism that we discuss in the following paper,[15] which is concerned with the (successful) use of locally defined functions as an expansion basis.

The CPA formalism employed for the present set of calculations is an example of what has been previously denoted arrangement channel quantum mechanics (ACQM).[16] It is the extension to bound states of the CCA formalism for scattering. The key ingredients in any multiparticle scattering theory are (a) inclusion of the full set of asymptotic boundary conditions corresponding to all arrangement channels or mass partitions of the scattering system and (b) a well-behaved system of equations from which the various transition amplitudes can in principle be obtained. The CCA theory or ACQM is a proper theory in the foregoing sense. (We shall use the acronyms CCA and ACQM interchangeably in the following discussions.) Since the formalism has been derived and discussed in many places, we simply summarize the relevant equations in the next section, which also deals with notation and approximation methods. Preliminary, highly abbreviated accounts of some of this work have previously appeared.[17]

II. THEORY

A. Notation

We consider a system of n distinguishable particles governed by a Hamiltonian $H=H_0+V$, where H_0 is the sum of kinetic energies and for simplicity V is a sum of two-particle interactions only. Identical particle symmetry will be introduced as needed. The Schrödinger equation is

$$(E-H)\Psi=0\ , \tag{2.1}$$

plus appropriate boundary conditions (BC). For E sufficiently large (and positive), the system can be observed in any of its asymptotic arrangement channels or mass partitions, which for the purposes of this paper are denoted by an index set with members $i,j,k,\ldots$. These range from the set S_2 of $N_2=2^{n-1}-1$ two-cluster or two-fragment channels to the unique n-particle breakup channel. Corresponding to each such arrangement channel j is a partitioning of H into a channel Hamiltonian H_j and a channel interaction V^j:

$$H=H_j+V^j\ , \tag{2.2}$$

where V^j is the sum of all intercluster interactions and $H_j=H_0+V_j$, where V_j is the sum of all the binding or intracluster interactions. Once H is specified, then H_j and V^j are determined through the partitioning of the n particles into the clusters defining the partition j.

The channel Hamiltonian H_j can always be separated into

$$H_j=K_j+h_j\ , \tag{2.3}$$

where K_j is the kinetic energy operator for relative motion of the clusters and h_j is the sum of Hamiltonians governing the internal states of the clusters. (In the Born-Oppenheimer approximation, the K_j are ignored; see below.) The eigenstates $\phi_j(\gamma)$ of h_j are of interest as an expansion basis; they obey

$$[\epsilon_j(\gamma)-h_j]\phi_j(\gamma)=0\ , \tag{2.4}$$

plus BC, where γ is the set of relevant quantum numbers. When all the clusters forming channel j are in bound states, we add the subscript b to γ, i.e., we use the symbol $\phi_j(\gamma_b)$ to denote a configuration of bound, noninteracting fragments. The collection of $\phi_j(\gamma_b)$ for each j forms the set of asymptotic states in channel j.

B. Review of ACQM

In ACQM, E and Ψ of Eq. (2.1) are obtained through solution of a set of coupled equations of wave-function components ψ_j. The specific equations of ACQM employed here are those of the channel permuting array form of the channel-coupling array theory. They may be written compactly as[7,16]

$$(E-H_j)\psi_j=V^{j+1}\psi_{j+1},\quad j=1,\ldots,N \tag{2.5}$$

plus BC, where, for the given value of N, $\psi_{j+N}=\psi_j$. When $E>0$, i.e., for scattering, it is sufficient[1] to obtain unique solutions if j runs over the members of S_2, that is, if $N=N_2=2^{n-1}-1$.

The fact that $\psi_{j+N}=\psi_j$ means that (2.5) can be reexpressed in explicit matrix form as

$$\begin{bmatrix} H_1 & V^2 & 0 & 0 & \cdots & 0 \\ 0 & H_2 & V^3 & 0 & & 0 \\ 0 & 0 & H_3 & & & 0 \\ 0 & 0 & & & & 0 \\ \vdots & \vdots & & & & \vdots \\ 0 & 0 & 0 & 0 & \cdots & V^N \\ V^1 & 0 & 0 & 0 & \cdots & H_N \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{bmatrix} \tag{2.6}$$

or equivalently

$$\underline{H}\vec{\psi}=E\vec{\psi}\ , \tag{2.7}$$

where the Hamiltonian-type operator $\underline{H}$ is obviously non-Hermitian.

The formal connection between these CPA equations and the Schrödinger equation (2.1) is obtained by summing both sides of (2.5) on j [or adding the rows of (2.6)]. This yields

$$\sum_j (E-H_j)\psi_j=\sum_j V^{j+1}\psi_{j+1}\ ,$$

which can easily be put in the form

$$(E-H)\sum_j \psi_j=0\ . \tag{2.8}$$

From (2.8) it follows that either (a) $\sum_j \psi_j=\Psi$, the solution to (2.1) corresponding to the Schrödinger eigenvalue E, or (b) $\sum_j \psi_j=0$, which defines a spurious solution.[14] The physical (Schrödinger) eigenvalues are thus embedded in the spectrum of $\underline{H}$ which also contains the spurious eigenvalues. Note that even though $\underline{H}^\dagger\neq\underline{H}$, the exact physical eigenvalues are real. The spurious eigenvalues are always trivially simple to identify (and thus discard) because the corresponding wave-function components always sum identically to zero. This identification holds for both the exact and any approximate spurious solutions, indeed it defines them uniquely. As we shall see in both this and the following paper, spuriosities in both approximate and exact calculations have been found.

C. Approximation techniques

There are two distinct types of approximation techniques which apply to the CPA equations. The first is called channel truncation. Solving (2.6) in its exact form requires the solution of at least N_2 coupled differential equations, making a practical calculation difficult for large values of N_2. Often, however, one can specify a set of channels which, based on physical reasoning and intuition, should not contribute significantly to a physical process over a given energy range. In a scattering problem for example, these might be the channels which are energetically closed. Or, in a bound-state problem those channels which have relatively little internal binding energy might be neglected as insignificant. For consistency, if the components in truncated channels are computed, they should have a small norm when compared with the previously retained components. Hence Eq. (2.6) can be simplified by excluding the presumed inconsequential channels. In this channel truncation approximation, the equations thus couple together only the retained channels. This approach is analogous to the coupled-channel approximation used in scattering theory; in practice its success will justify its application. Levin and Krüger[10] first successfully used this approximation technique for the H_2 molecule.

A second useful approximation technique involves the Galerkin-Petrov method.[18,19] Let $\vec{\psi}$ be a formal solution to (2.7). Then for an arbitrary complete orthonormal set $\{\vec{u}_n\}$ in the asymptotic space, one may express $\vec{\psi}$ in terms of the $\vec{u}_n$, as follows:

$$\vec{\psi}=\lim_{M\to\infty}\sum_{n=1}^{M} a_n\vec{u}_n \; . \tag{2.9}$$

The coefficients a_n can be found using a slight generalization of the usual definition of inner product:

$$(\vec{u}_m \mid \vec{u}_n)\equiv\sum_j \langle u_{m,j} \mid u_{n,j}\rangle=\delta_{mn} \; , \tag{2.10}$$

where the $\mid\vec{u}_n)$ is a column vector of kets with jth element $\mid u_{n,j}\rangle$ and $(\vec{u}_m\mid$ is a row vector of bras with ith element $\langle u_{m,i}\mid$. The sum on j in (2.10) is over all partitions included in the calculations.

Equations (2.9) and (2.10) may be used to transform (2.7) into

$$(\vec{\phi}\mid(\underline{H}-E\mathbb{1})\mid\vec{\psi})=\lim_{M\to\infty}\sum_{n=1}^{M}(\vec{\phi}\mid(\underline{H}-E\mathbb{1})\mid\vec{u}_n)a_n=0 \; , \tag{2.11}$$

which holds for arbitrary $\vec{\phi}$ in the asymptotic space. The Galerkin method proceeds in two steps from (2.11). First, a new equation is defined which will be solved exactly:

$$\sum_{n=1}^{M}(\vec{\phi}\mid(\underline{H}-E^{(M)}\mathbb{1})\mid\vec{u}_n)a_n^{(M)}=0 \; . \tag{2.12}$$

The new quantities, $E^{(M)}$ and $a_n^{(M)}$, which generally depend on the value of M, are obtained when (2.12) is satisfied. Equation (2.12) is taken to have meaning for arbitrary $\vec{\phi}$. In order to specify $a_n^{(M)}$ and transform (2.12) into an algebraic eigenvalue problem, $\vec{\phi}$ is equated in turn to each of the M vectors $\vec{u}_n$, $n=1,2,..,M$:

$$\sum_{n=1}^{M}(\vec{u}_m\mid(\underline{H}-E^{(M)}\mathbb{1})\mid\vec{u}_n)a_n^{(M)}=0 \; . \tag{2.13}$$

This result is a rank-M algebraic eigenvalue problem. In applying the method to ACQM bound-state problems, we can invoke several important theorems.[18] First, the limit point of each convergent sequence of eigenvalues $E^{(1)}, E^{(2)}, \ldots, E^{(k)}, \ldots$ is an eigenvalue of $\underline{H}$ and all such sequences converge. Second, the associated vector sequence

$$\left\{\sum_{n=1}^{M} a_n^{(M)}\vec{u}_n\right\}_{M=1}^{\infty}$$

converges (strongly in norm) to the corresponding eigenvector $\vec{\psi}$. Finally, the entire spectrum of $\underline{H}$ can be determined in this manner. At no point does this method require the constraint that $\underline{H}$ be Hermitian, thus making the Galerkin-Petrov method a fairly general approach. Of course, alternate approaches to discretize partial differential equations do exist. However, the one most commonly used, viz., the Rayleigh quotient method,[20] cannot be applied in the present problem due to the non-Hermiticity of $\underline{H}$. On the other hand, the Galerkin method subsumes the Rayleigh quotient method. Generally the next step in the Galerkin formulation is to reduce the continuity class required of the $\vec{u}_n$, arriving at a set of equations involving a lower order of differentiation.[19] This is not necessary for our purposes here.

In the molecular bound-state calculations presented below, the Schrödinger Hamiltonian is evaluated in the Born-Oppenheimer approximation. The justification of this approximation has been thoroughly studied in quantum mechanics as applied to the Schrödinger equation. The rationale for its use in ACQM is the relation $\sum_j\psi_j=\Psi$ between the physical solutions of the arrangement channel equations and the solutions of the Schrödinger equation using the Born-Oppenheimer Hamiltonian.

III. CALCULATIONS

A. $H_2{}^+$

The Hamiltonian of the hydrogen molecular ion ($H_2{}^+$) in the Born-Oppenheimer approximation[21] is

$$H=-\tfrac{1}{2}\nabla^2-\frac{1}{\mid\vec{r}_A\mid}-\frac{1}{\mid\vec{r}_B\mid}+\frac{1}{R} \; . \tag{3.1}$$

Here, two stationary protons separated by a distance R interact with an electron positioned at a distance $\vec{r}_A$ from proton A and $\vec{r}_B$ from proton B. In this approximation, the bound-state problem which initially involves three interacting particles has been reduced to a one-electron problem by freezing out the nuclear motion with the result that the reduced Schrödinger equation may be solved analytically.[21,22] We stress here that the reduced ACQM equation derived below is also a one-electron problem (but without a known analytic solution) which is derived from a three-particle Hamiltonian using a many-particle collision formalism.

There are two 2-cluster partitions for this system, and the Hamiltonian (3.1) can be partitioned in two ways corresponding to these channels:

$$H=H_1+V^1=\left[-\tfrac{1}{2}\nabla^2-\frac{1}{\mid\vec{r}_A\mid}\right]+\left[\frac{1}{R}-\frac{1}{\mid\vec{r}_B\mid}\right] \tag{3.2}$$

and

$$H=H_2+V^2=\left[-\tfrac{1}{2}\nabla^2-\frac{1}{\mid\vec{r}_B\mid}\right]+\left[\frac{1}{R}-\frac{1}{\mid\vec{r}_A\mid}\right] . \tag{3.3}$$

H_1 physically corresponds to an isolated hydrogen atom formed from A and the electron, while V^1 represents the electrostatic field experienced by the second proton. By the rules of vector addition

$$R^2=r_A^2+r_B^2-2\vec{r}_A\cdot\vec{r}_B$$

$$=r_B^2\left[1-2\frac{\vec{r}_A\cdot\vec{r}_B}{r_B^2}+\frac{r_A^2}{r_B^2}\right].$$

For the case $r_A^2 \ll r_B^2$,

$$V^1=\frac{1}{R}-\frac{1}{|r_B|}\cong\frac{\vec{r}_A\cdot\vec{r}_B}{r_B^3},\quad \frac{r_A^2}{r_B^2}\ll 1 .$$

Hence V^1 (and similarly V^2) fall off as an electrostatic dipole and is therefore short range and integrable (in the analytic sense used in Ref. 2).

The arrangement channel equations for this problem are (uniquely) given by

$$\begin{bmatrix} H_1 & V^2 \\ V^1 & H_2 \end{bmatrix}\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}=E\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}. \tag{3.4}$$

From the definitions (3.2) and (3.3) it is easy to show that $P_{AB}H_1P_{AB}=H_2$ and $P_{AB}V^1P_{AB}=V^2$, where P_{AB} is the proton interchange operator. As discussed in Refs. 8 and 10, one can use this property to reduce (3.4) to decoupled equations, one for $\psi_1+P_{AB}\psi_2$ and one for $\psi_1-P_{AB}\psi_2$, but it is simpler to require (as one may do without loss of generality) that

$$\psi_1^{\pm}(\vec{r}_A,\vec{r}_B)=P_{AB}\psi_2^{\pm}(\vec{r}_A,\vec{r}_B)$$

$$=\pm\psi_2(\vec{r}_B,\vec{r}_A). \tag{3.5}$$

The $(+)$ sign gives a *gerade* state while the $(-)$ sign yields an *ungerade* one,[8,21] through the relation $\psi=\psi_1+\psi_2$. Equivalently, one may solve (3.4), seeking those solutions which lead to the proper symmetry. We follow this latter procedure, since it will lead (in the local basis calculations of the following paper) to simpler equations to solve. We note that for the *gerade* case use of (3.5) in (3.4) yields, as in I, an equation identical in form to that of Mann and Privman,[23] which is derived from a primitive function formulation. However, this relationship between the ACQM approach and that of the primitive function in the H_2^+ *gerade* case is not maintained for the H_2^+ *ungerade* case nor for the general, multiparticle ACQM equations, which do not reduce to a single decoupled equation on application of invariance group procedures.

Equation (3.4) can be formally solved using the Galerkin method by expanding ψ_1 and ψ_2 in a complete set of functions. Since the channel partitioning separates the system into an H atom and a proton, it is reasonable to employ the hydrogenic states as a basis. There are two reasons for doing this. First, the numerical calculation is simplified when each expansion function is an eigenfunction of the channel Hamiltonians H_1 or H_2 even though for computational reasons, the continuum must be neglected. Second, $\psi_i(R)$ asymptotically evolves (as $R\to\infty$) to a hydrogenic state in channel i (and vanishes in channels $j\neq i$). Thus this expansion set is the natural one to choose in the spirit of perturbation theory. However, just as it is known from calculations based directly on the Schrödinger equation, one cannot expect a single-cluster basis to describe the channel components uniformly well at small values of R, for which the contributions of the off-diagonal elements of $\underline{H}$ cannot be neglected. Indeed, the failure of a single-center basis when computing the channel components is an indirect measure of the contribution to the total wave function of interchannel mixing. This will become an important consideration in multichannel calculations.

TABLE I. Initial results for the H_2^+ ground state.

	R_e (a_0)	$E(R_e)$ (a.u.)
Schrödinger equation		
Perturbation[a]	2.50	-0.5654
Scaled variational[b]	2.02	-0.5871
Exact[c]	2.000	-0.60263
Arrangement channel		
1*s* Galerkin[d]	2.07	-0.6132
1*s* Galerkin scaled	1.86	-0.6196

[a] Reference 21.
[b] Reference 24.
[c] Reference 25.
[d] Reference 8.

In the simplest ACQM calculation[8] only the 1*s* state of hydrogen was retained, yielding the following expression for the *gerade* ground state of the molecule:

$$E^+(R)=-\frac{1}{2}+\left[\frac{1}{R}-\frac{2}{3}R\right]e^{-R}. \tag{3.6}$$

In Table I this result is contrasted with other calculations. In particular, by using the 1*s* state as the perturbation wave function and beginning with the Schrödinger equation[21] the ground-state energy was found to have a minimum value of -0.565 a.u. and an equilibrium value R_e of R of $2.50a_0$. This calculation essentially uses the same wave-function input as the arrangement channel calculation leading to (3.6) yet gives inferior results for R_e and $E(R_e)$. Although the accuracy of the computed energy is not necessarily a sensitive test of the accuracy of the molecular wave function it is nevertheless one important measure and the relative accuracy of this arrangement channel calculation merits a closer examination.

Because the Hamiltonian (3.1) is Hermitian, the variational-minimum principle may be applied to improve the Schrödinger equation perturbation calculation above. By introducing an exponential scale factor into the 1*s* wave function, the values of R_e and $E(R_e)$ can be easily improved to be $2.02a_0$ and -0.587 a.u., respectively.[24] Since the arrangement channel operator $\underline{H}$ is not Hermitian, the corresponding variational theorem does not produce a minimum principle. This explains why, for example, the calculated value of $E(R_e)$ in Table I [found using Eq. (3.6)] lies below the exact value computed by Wind.[25] Nevertheless in an attempt to mimic the Schrödinger equation variational calculation an energy has been com-

TABLE II. Hydrogenic expansion for the H_2^+ ground state.

Expansion	Rank	$E(R=1.90a_0)$ (a.u.)
$1s$	1	-0.6107
$1s2s$	2	-0.6168
$1s2s3s$	3	-0.6181
$1s\ldots6s$	6	-0.6187
$1s\ldots2p$	7	-0.6251
$1s\ldots5p$	10	-0.6279
$1s\ldots6p$	11	-0.6286
$1s\ldots3d$	12	-0.62854
$1s\ldots6d$	15	-0.62853
$1s\ldots4f$	16	-0.62853
$1s\ldots6h$	21	-0.62853
Exact[a]	$R=2.00a_0$	-0.60264 a.u.

[a] Reference 25.

TABLE III. Hylleraas-Shull-Löwdin expansion for the H_2^+ ground state.

Expansion	Rank	$E(R=1.92a_0)$ (a.u.)
$1s$	1	-0.6116
$1s2s$	2	-0.6089
$1s2s3s$	3	-0.6114
$1s\ldots6s$	6	-0.6109
$1s\ldots2p$	7	-0.6154
$1s\ldots5p$	10	-0.6111
$1s\ldots6p$	11	-0.6131
$1s\ldots3d$	12	-0.6070
$1s\ldots6d$	15	-0.6041
$1s\ldots4f$	16	-0.6053
$1s\ldots6f$	18	-0.60970
$1s\ldots6g$	20	-0.60966
$1s\ldots6h$	21	-0.61007
Exact[a]	$R=2.00a_0$	-0.60264 a.u.

[a] Reference 25.

puted using Eq. (3.4) and the channel component ansatz

$$\psi_1(\zeta)=\left[\frac{\zeta^3}{\pi}\right]^{1/2}e^{-\zeta r_A}\,, \tag{3.7}$$

with a similar form for channel two. The energy functional computed using (3.7) is stationary at $\zeta=1.11$ but the corresponding R_e and $E(R_e)$ become considerably worse, as seen in Table I.

These ACQM results, plus those of Ref. 8 for the *ungerade* state, clearly indicate the need for further investigations. Loss of the variational minimum principle is discomforting since normally in quantum mechanics a minimum principle guarantees that the exact energy level lies below (or is equal to) any approximate one for a given Hamiltonian. No similar guidelines yet exist for ACQM, making it a more problematic theory with which to perform approximate calculations. In addition, we recall that ACQM was conceived as a scattering theory, so that certain results have only been *inferred* to hold for the bound-state case. In particular, the point spectrum of $\underline{H}$ has been assumed to contain the point spectrum of H based on analytic continuation from the $E>0$ case to the $E<0$ one (see I). Yet, in the calculations presented above there is as yet no indication that an H_2^+ ground state calculated using ACQM will indeed be the physical one. It is clear therefore that more extensive calculations of H_2^+ would prove useful from a formal point of view.

An extended calculation of the H_2^+ ground state was first performed using additional (bound) hydrogenic states. The discrete hydrogen states are defined by[26]

$$\eta_{nlm}(\vec{r})=N_{nl}\left[\frac{2r}{n}\right]^{l}e^{-r/n}L_{n-l-1}^{2l+1}\left[\frac{2r}{n}\right]Y_{lm}(\theta,\phi)\,, \tag{3.8}$$

where N_{nl} is a normalization constant, $Y_{lm}(\theta,\phi)$ is a spherical harmonic, and L_{n-l-1}^{2l+1} is an associated Laguerre polynomial.[20] Although the set of states (3.8) for n ranging from 0 to ∞, $0<l<n$, and $|m|<l$, are well known not to be complete in the Hilbert space of twice differentiable, square integrable functions,[27] a sequence of calculations using (3.8) has been carried out, the results of which are summarized in Table II. In the table emphasis has been placed upon the value of the energy at $R=1.90a_0$ which corresponds to the point of minimum energy in the rank twenty-one case. The calculations proceeded by first expanding in S states over the range $1\leq n\leq 6$, then in P states, D states, etc., until the calculation contained all allowed angular momentum states in the first six shells, totalling twenty-one in number. With the use of this expansion technique the value of the equilibrium energy grows steadily worse dropping well below the known exact result until the twelve-term case. Then this trend alters and the energies very slowly improve. Calculations were not extended beyond the twenty-one—term case since improvement was so slow. Furthermore, since the effect of neglecting the continuum states could not be ascertained independently, a lack of convergence could be due to the choice of expansion functions.

To investigate the role the continuum might play in the preceding calculations, a different expansion basis was used next, one which is complete without continuum contributions. These are the Hylleraas-Shull-Löwdin functions Λ_{nlm} defined by[28]

$$\Lambda_{nlm}(\vec{r})=N'_{nl}(2r)^{l}e^{-r}L_{n-l-1}^{2l+1}(2r)Y_{lm}(\theta\phi)\,. \tag{3.9}$$

In addition to being complete, this discrete set of functions has the advantage that the exponential factor in (3.9) is independent of the index n, in contrast to the hydrogenic states whose exponent varies as $-r/n$. Thus the set (3.9) is expected to converge more rapidly than the set (3.8). In Table III are listed the results of our calculation using (3.9) as the expansion basis. The equilibrium separation of the twenty-one—term expansion is computed to be $1.92a_0$ and all other energies listed have been quoted at that value. This equilibrium separation is a small improvement over that found using the discrete hydrogen states as a basis. Examining Table III one sees that the energies oscillate as the number of terms included grows from one (which is the simple hydrogenic 1*s* calculation), to twenty-one, which includes all states such that $n<6$, $0<l<n$. Furthermore, the energy is always *below* the exact result of Wind.[23] Compared to the hydrogenic expansion, however, the improvement is significant. Again calculations were not extended beyond the twenty-one—term case, since the slow oscillations indicate a not rapid convergence, typical of three-body Faddeev Coulomb calculations.[6] Instead of pursuing this slowly converging globally defined basis type of calculation further for $H_2{}^+$, we use a locally defined basis in the following paper to obtain truly converged results.

The preceding sets of results and comments refer to the *gerade* ground state. The ACQM calculations also yielded *ungerade* energy surfaces. All of them were unphysical in the sense that as $R\to 0$, each *ungerade* potential-energy curve approached $-\infty$, exactly as in the original Krüger-Levin computations.[8] This is a further impetus for the more detailed (and converged) study described in the following paper.

B. H_2

The hydrogen molecule is a system of two protons and two electrons. In the Born-Oppenheimer (BO) approximation the motion of the protons is frozen and their coordinates enter parametrically in the wave function. Expressed in the center-of-mass frame only the interproton coordinate R has relevance. The BO Hamiltonian is[21]

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+\frac{1}{r_{12}}-\frac{1}{r_{A1}}-\frac{1}{r_{B2}}-\frac{1}{r_{A2}}-\frac{1}{r_{B1}}+\frac{1}{R}\ , \tag{3.10}$$

where numerical indices label the electronic coordinates and the alphabetic ones label the proton coordinates, e.g., r_{A1} is the distance between proton A and electron 1. Our main interest is in computing the low-lying spin-singlet states within an ACQM formulation beginning with the Hamiltonian (3.10) and so further probing the applicability of ACQM to realistic systems. We also are interested in the behavior of the spin-triplet states, which are the analog of the $H_2{}^+$ *ungerade* states. First, however, we recall some of the approximate solutions to the Schrödinger equation corresponding to this Hamiltonian. An exact analytical solution of the Schrödinger equation is not available due to the electron-electron repulsion term contained in (3.10) but there do exist many numerically exact treatments of the problem. For our purposes the results of Kolos and Roothaan[29] are sufficiently accurate; they obtained a ground-state proton equilibrium separation of $R_e=1.401a_0$ and an energy minimum of -1.1744 a.u. These results are obtained via a fifty-term variational calculation. Less complex (and less accurate) calculations for the H_2 ground state have been performed beginning with the valence-bond model of Heitler and London.[30] In their approximation, the H_2 (covalent) bond is due to the sharing of the two electrons between the two hydrogen atoms. In the ground-state configuration the Heitler-London variational wave function assumes a covalent form, i.e.,

$$\psi^{\rm VB}\propto\eta_{100}(\vec{r}_{A1})\eta_{100}(\vec{r}_{B2})+\eta_{100}(\vec{r}_{A2})\eta_{100}(\vec{r}_{B1})\ . \tag{3.11}$$

With this form as the zero-order wave function a perturbation calculation yields $R_e=1.65a_0$ and an equilibrium energy of 1.115 a.u. This calculation was subsequently improved upon by Wang,[31] who introduced an exponential (variational) scale factor into the 1*s* orbital with which he minimized the energy functional. One other calculation of interest is the Hartree-Fock self-consistent-field computation of Kolos and Roothaan.[29] The interproton equilibrium separation and the equilibrium-point energy for the H_2 ground state for each of these calculations are summarized in Table IV.

TABLE IV. Ground state (singlet) calculations for H_2.

Schrödinger equation	R_e (a_0)	$E(R_e)$ (a.u.)
Heitler-London[a]	1.65	−1.115
Scaled variational[b]	1.44	−1.138
Hartree-Fock[c]	1.40	−1.134
Exact[c]	1.401	−1.1744
Arrangement channel 1*s* Galerkin	1.42	−1.163

[a] Reference 30.
[b] Reference 31.
[c] Reference 29.

The ACQM equations for the H_2 problem are derived from the Hamiltonian (3.10) for which there are six two-cluster-channel partitions.[10] In physical terms there are two equivalent H + H channels, two equivalent $H^+ + H^-$ channels and two equivalent $H_2{}^+ + e$ channels. Hence the arrangement channel operator $\underline{H}$ is a rank-six, operator-valued matrix. The exact ACQM formulation accordingly requires the solution of six coupled second-order partial differential equations. Although the numerical solution of the full ACQM problem is feasible using modern computers, it is nevertheless desirable to reduce the complexity of the problem. Doing so one can hope to expose practical and interpretation details of the theory. A reduction of the number of coupled equations via the method of channel truncation obviously makes the problem more manageable. A truncation of the set of channels can be effected by hypothesizing a physical model in which only certain two-cluster channels are important. A measure of the success of the assumed model is the accuracy of at least some of the resultant solutions of the (truncated) approximate equations. For the H_2 calculation we begin with the Heitler-London model, i.e., two equivalent H + H channels[10]; the other four are discarded. This model of the H_2 ground state is both intuitively pleasing and simple and is also computationally practical, since the 6×6 matrix operator $\underline{H}$ is approximated by a 2×2 operator-valued matrix. In other words, the set of six coupled equations is reduced to a set of two coupled equations:

$$\begin{aligned}&H_1\psi_1+V^2\psi_2=E\psi_1\ ,\\&H_2\psi_2+V^1\psi_1=E\psi_2\ ,\end{aligned} \tag{3.12}$$

where

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{r}{r_{A1}} - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}\ , \tag{3.13a}$$

$$V^1 = \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}}\ , \tag{3.13b}$$

and

$$\begin{aligned} H_2 &= -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{B1}} - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A2}}\ , \\ V^2 &= \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{B2}}\ . \end{aligned} \tag{3.14}$$

The eigenvalue E in (3.12) will be an approximation to the eigenvalue of (3.10) provided that the approximations used for ψ_1 and ψ_2 do not yield $\psi_1+\psi_2=0$.

It follows from (3.13) and (3.14) that channel (1) consists of the two (noninteracting) hydrogen atoms $(A1)$ and $(B2)$, while in channel (2) we have $(A2)$ and $(B1)$. Since the intercluster interaction V^j falls off as R^{-2} for large R and H_j describes two noninteracting hydrogen atoms, then ψ_j is most naturally approximated by a finite sum of products of hydrogenic states, i.e.,

$$\psi_1(\vec{r}_1,\vec{r}_2) \cong \sum_{\alpha,\beta} C_{\alpha\beta}\eta_\alpha(\vec{r}_{A1})\eta_\beta(\vec{r}_{B2}) \tag{3.15}$$

and

$$\psi_2(\vec{r}_1,\vec{r}_2) \cong \sum_{\lambda,\mu} D_{\lambda\mu}\eta_\lambda(r_{B2})\eta_\mu(r_{A1})\ , \tag{3.16}$$

where α, β, λ, and μ denote the three hydrogenic quantum numbers (nlm) and C and D are expansion constants. It is not hard to show[10] that because of the equivalence of the nuclear centers, which upon interchange transform H_1 into H_2 and V^1 into V^2, no loss of generality is incurred if one takes $\lambda=\alpha$ and $\mu=\beta$ in (3.15) and (3.16). Furthermore, the approximation to Ψ, given by $\Psi=\psi_1+\psi_2$, will have the spatial symmetry corresponding to spin singlet (triplet) if in (3.16) we choose $D_{\alpha\beta}=C_{\alpha\beta}$ $(-C_{\alpha\beta})$. Denoting spin singlet (triplet) by a superscript $+$ $(-)$, we then have

$$\psi_1 \cong \sum_{\alpha,\beta} C_{\alpha\beta}\eta_\alpha(r_{A1})\eta_\beta(r_{B2})\ , \tag{3.17}$$

$$\psi_2^{\pm} \cong \pm\sum_{\alpha,\beta} C_{\alpha\beta}\eta_\alpha(r_{B1})\eta_\beta(r_{A2})\ , \tag{3.18}$$

and

$$\Psi^{\pm} = \psi_1 + \psi_2^{\pm} \cong \sum_{\alpha,\beta} C_{\alpha\beta}(1\pm P_{AB})\eta_\alpha(r_{A1})\eta_\beta(r_{B2})\ . \tag{3.19}$$

All the α and β sums in (3.17)—(3.19) are assumed to run only over a finite set of bound-state quantum numbers. Note that if $\alpha=\beta=100$ in (3.19), then the resulting Ψ^+ is precisely Ψ^{VB} of Heitler and London [Eq. (3.11)]. The R_e and $E^+(R_e)$ values that result from an ACQM calculation using such an ansatz for ψ_1 and ψ_2^+ are quite different and much more accurate than the Heitler-London results, as indicated by the 1*s* Galerkin row in Table IV. Even the calculation of Wang,[31] which yields the variationally best wave function having the general Heitler-London product form, is less accurate than the approximate 1*s* ACQM solution. The ACQM energy is also superior to the Hartree-Fock calculation, indicating that the arrangement channel approach inherently includes a significant amount of the correlation energy. The success of the Levin-Krüger calculation warrants a more detailed calculation in order to investigate, if nothing else, the limits of the approximations (3.17)—(3.19).

TABLE V. Extended ACQM calculations for the H_2 ground state.

Hydrogenic states	Rank	R_e (a_0)	E_e (a.u.)
$(1s)^2$	1	1.42	-1.1630
$1s, 1s\text{-}2s$	2	1.40	-1.1637
$(1s\text{-}2s)^2$	4	1.40	-1.1646
$(1s\text{-}2s\text{-}2p)^2$	7	1.40	-1.1639
$(1s\text{-}2s\text{-}3s)^2$	9	1.40	-1.1647
Exact[a]		1.401	-1.1744

[a] Reference 29.

A straightforward extension of the Levin-Krüger calculation has been carried out by allowing the α and β sums in (3.17) and (3.18) to range over various values of n and l. The magnetic quantum number m was set equal to zero since our interest was in determining the ground state and those excited states having zero rotational angular momentum. Owing to the mapping properties between channels (1) and (2), Eq. (3.12) can be reexpressed as a single equation involving a nonlocal two-center exchange operator.[10] Since integrals involving the functions η_{nlm} and this exchange operator can be easily performed, the actual problem solved is one involving a single equation with only local operators thereby reducing the difficulty of the resultant algebraic eigenvalue problem. The singlet ground state values of R_e and $E_e=E^+(R_e)$ for a variety of expansions are listed in Table V. Examining the terms in the energy column it is apparent that the convergence is oscillatory: e.g., when the 2*p* states are included in addition to the 2*s* states, the energy minimum is elevated. This behavior is anticipated when dealing with non-Hermitian equations, as noted above. It is also apparent from Table V that the exact minimum is being approached very slowly. [We do not display and compare with the exact Kolos-Roothaan curve[29] even the most accurate of our $E^+(R)$ potential-energy curves, since it is not visually different than the 1*s*,1*s* CCA curve of Ref. 10.] Although slow convergence properties are familiar to expansions using hydrogenic states, as already noted, it is possible that at equilibrium the ionic configurations play a small but essential role. In that case, even an exact solution of (3.12) would not provide an adequate description of the H_2 ground state. Examination of the difference between E_e for greatest rank ACQM calculation and for the exact calculation suggests that approximately 1% of the ground-state energy is ionic in origin. This is consistent with the conclusion based on a Schrödinger equation energy computation.[21]

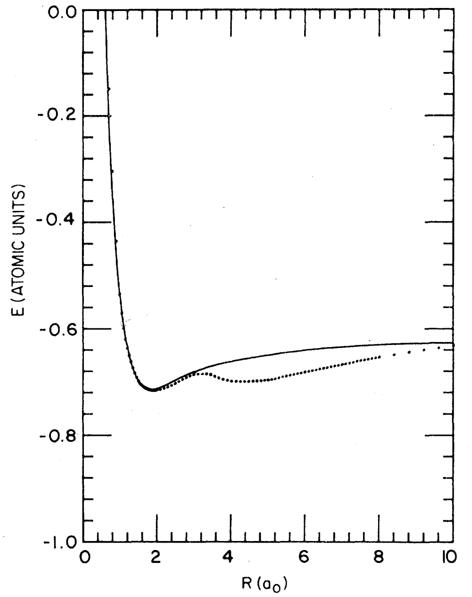

FIG. 1. First excited $E\,{}^1\Sigma_g^+$ potential-energy curves for H_2. Dotted line from Davidson (Ref. 32), solid line is the ACQM result based on a four-state $(1s\text{-}2s)^2$ expansion of ψ_1.

Since the Galerkin-Petrov procedure is one of matrix diagonalization, it yields approximations to excited states having the same wave-function symmetry as the ground state. Among these is the first excited $E\,{}^1\Sigma_g^+$ state. An accurate energy curve for this state has been computed by Davidson[32] who used a variational-method approach to approximate the solution of the Schrödinger equation for H_2. He found two minima in this curve, the first at $R=1.9a_0$ and $E=-0.7162$ a.u. and the second at $R=4.2a_0$ and $E=-0.7007$ a.u. In the variational calculation a twenty configuration covalent wave function is necessary to determine the inner minimum accurately while a twenty configuration ionic wave function is necessary for the outer minimum. The resultant energy curve is displayed as the dotted curve in Fig. 1. The ACQM energy curve computed by expanding (3.17) and (3.18) in only the $1s$ and $2s$ hydrogenic orbitals is shown in the figure as the solid curve. Although the ionic minimum is totally absent in the ACQM calculation, the covalent minimum is quite accurately represented with only these four terms. A larger hydrogenic basis diagonalization for (3.12) has been performed with the results for R_e and E_e for the excited state indicated in Table VI. The equilibrium separation and energy tend to oscillate and converge slowly as the number of states is increased as was the case for the ground state. No attempt to optimize the choice of expansion states has been made in either case. The fact that the ionic minimum is totally lost is almost certainly a consequence of the channel truncation, since the retained $H+H$ channels unlike the nonretained $H+H^+$ or $H_2^+ + e$ channels, have no ionic character. Rather than regard this as a deficiency, however, the nonappearance of the ionic minimum exemplifies how ACQM might be useful in analyzing quantum states. The chemical bond can be computationally probed via ACQM to ascertain the significance of the constituent wave-function components simply by solving relevant truncated sets of arrangement channel equations. Furthermore, this technique of analysis relies solely upon the choice of Hamiltonian partitioning and is independent of the choice of wave-functional form. Such analyses are currently in progress and will be reported on in a subsequent communication.[33]

TABLE VI. First excited $H_2\,{}^1\Sigma_g^+$ state covalant minimum.

Hydrogenic states	Rank	R_e (a_0)	E_e (a.u.)
$1s, 1s\text{-}2s$	2	1.90	-0.6042
$(1s\text{-}2s)^2$	4	1.85	-0.7142
$(1s\text{-}2s\text{-}2p)^2$	7	1.90	-0.7135
$(1s\text{-}2s\text{-}3s)^2$	9	1.85	-0.7144
Exact[a]		1.9	-0.7162

[a]Reference 32.

As is evident from Fig. 1, the $E\,{}^1\Sigma_g^+$ energy curve has the proper physical behavior. It is identified in the calculation as the first excited state because in the separated atom limit, the (asymptotic) energy is 1.25 a.u. The higher-energy excited states produced by the Galerkin-Petrov diagonalization procedure can be similarly identified by asymptotic energies. We display in Fig. 2, over the range $0 \le R \le 10a_0$, the general form of the single energy curves arising from the $(1s2s)^2$ calculation that produced the previous $E\,{}^1\Sigma_g^+$ state. Three of these curves correspond to an approximate Ψ $(=\psi_1+\psi_2)$ having *gerade* symmetry, while the fourth has *ungerade* symmetry. All are seen to behave correctly at $R=0$ and to go asymptotically to values corresponding to the energies of those hydrogenic states which, via the approximation, represent the separated atom (noninteracting) system. This feature, in which the ψ_j yield the proper dissociation limit, is one of the advantages of working with the ACQM formalism. Another is the relative ease of calculation which allows one to generate relatively accurate approximations to many states. Of course, one must also satisfy the condi-

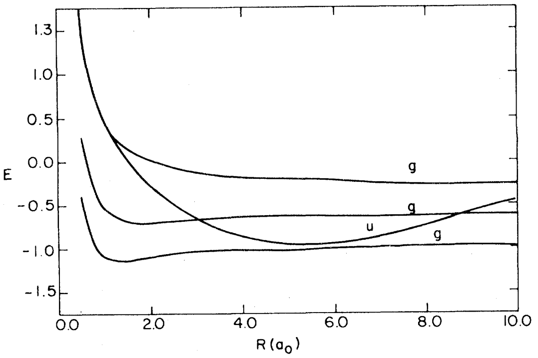

FIG. 2. Comparison of the first four ${}^1\Sigma_g^+$ H_2 potential-energy curves calculated from ACQM using the four-state expansion of Fig. 1.

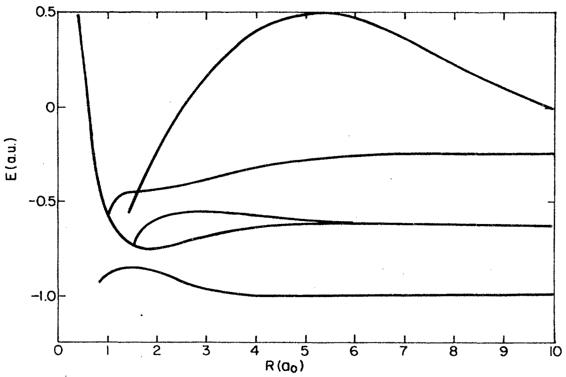

FIG. 3. Behavior of the four nonphysical and the one physical H_2 triplet potential-energy curves arising from a five-state, $(1s\text{-}2s)^2(2p_0)^2$ ACQM calculation.

tion that the $E(R)$ be physically well behaved, as is true in the present instance of H_2 singlet states or the previous determined ${H_2}^+$ *gerade* states. This condition is not always satisfied in the case of the H_2 triplet states, which we examine next.

The triplet states are obtained by using expansion (3.18) with the negative sign. We have carried out a series of calculations corresponding to the ranks 4 and 7 ones of Table VI. Triplet potential energy curves $E^-(R)$ are shown in Figs. 3 and 4. The five curves of Fig. 3 were calculated using a five-state basis $(1s2s)^2$,$[(2p)^2]$, and it is obvious that only one of the five has the correct $R\rightarrow 0$ and $R\rightarrow\infty$ physical behavior. This curve is one whose approximate Ψ $(=\psi_1+\psi_2)$ is of the form $C_{1s2s}[\eta_{1s}(r_{A1})\eta_{2s}(r_{B2})+\eta_{1s}(r_{B1})\eta_{2s}(r_{A2})]$ plus a $[(2p)^2]$ term. As such, this approximate wave function does not vanish at $R=0$, and thus gives no hint of being a spurious solution [i.e., limit $R\rightarrow 0$ $(\psi_1+\psi_2)\neq 0$]. On the other hand, each of the $\psi_1+\psi_2$ for the four physically incorrect $E^-(R)$ are such that limit $R\rightarrow 0$ $(\psi_1+\psi_2)=0$, and this behavior is a clear indication that the corresponding $E^-(R)$ will manifest unphysical behavior at $R=0$, as indeed they do. We shall examine the problem of these physically incorrect energy curves in more detail in the following paper,[15] where we also provide a solution to the problem.

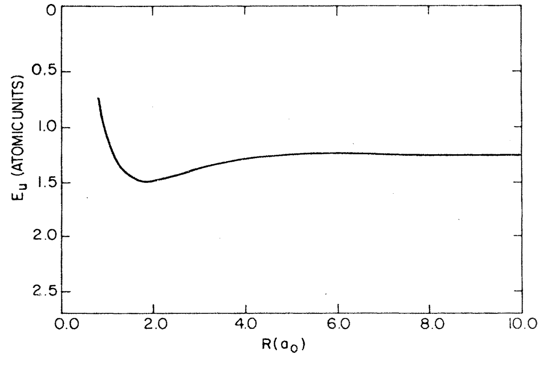

FIG. 4. Behavior of the one physical H_2 triplet potential-energy curve arising from a four-state, $(1s2s)^2$ ACQM calculation. This is essentially indistinguishable from the analogous result shown in Fig. 3.

TABLE VII. Helium-hydride calculations.

	R_e (a_0)	$E(R_e)$ (a.u.)
Schrödinger equation		
Exact[a]	1.46	-2.9787
Arrangement channel		
Two channel	1.1	-2.7973
Three channel	1.49	-2.9242

[a]Reference 34.

As a final point, we note that Fig. 4 shows for a four-state calculation essentially the same physically correct $E^-(R)$ as in the results of the five-state computation displayed in Fig. 3. The large range of R indicates the basic lack of structure in this computed $E^-(R)$ beyond the single broad minimum around $1.9a_0$.

C. HeH^+

The helium hydride ion, HeH^+, can be considered as a prototype nonhomopolar diatomic molecule. As a two-center, two-electron problem it is not dissimilar to the hydrogen molecule. Its Hamiltonian in the Born-Oppenheimer approximation is

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+\frac{2}{R}+\frac{1}{r_{12}}-\frac{2}{r_{A1}}-\frac{1}{r_{B1}}-\frac{2}{r_{A2}}-\frac{1}{r_{B2}}\,, \tag{3.20}$$

using the notation established in the H_2 calculation. The doubly charged helium nucleus is taken as center A. Kolos and Peek[34] computed the ground-state solution to the Schrödinger equation corresponding to the Hamiltonian (3.20) using the variational method. With an eighty-three—term variational wave function they found a total energy of $-2.978\,69$ a.u. at an equilibrium internuclear separation of $1.4632a_0$. This result is considered exact for our purposes and will be used for comparisons.

As in the hydrogen molecular case the Hamiltonian (3.20) supports six two-channel partitions: $He^{2+}+H^-$, $He+H^+$, $HeH^{2+}+e^-$, and He^++H, with the last two groupings each representing two equivalent channels due to the identity of the electrons. Since the nuclear centers are dissimilar this molecule affords us an opportunity to further test the concept of channel truncation. This is also the first molecule encountered which will require at least a three-channel calculation to obtain accurate results.

The three channels with the greatest internal binding energies are the $He+H^+$ and the two He^++H ones. As a first attempt we shall omit from Eq. (2.6) all but the latter two channels. Then the calculation can be carried out in analogy to the ${H_2}^+$ and H_2 cases. The channel operators are

$$
\begin{aligned}
H_1 &= -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{r_{B1}} - \frac{2}{r_{A2}} \,, \\
V^1 &= \frac{2}{R} + \frac{1}{r_{12}} - \frac{2}{r_{A1}} - \frac{1}{r_{B2}} \,,
\end{aligned} \tag{3.21}
$$

and

$$
\begin{aligned}
H_2 &= -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}} - \frac{2}{r_{A1}} \,, \\
V^2 &= \frac{2}{R} + \frac{1}{r_{12}} - \frac{1}{r_{B1}} - \frac{2}{r_{A2}} \,.
\end{aligned} \tag{3.22}
$$

The truncated arrangement channel equations are, in matrix form,

$$
\begin{bmatrix} H_1 & V^2 \\ V^1 & H_2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} . \tag{3.23}
$$

As in Secs. III A and III B, it is simplest to represent the channel components in terms of their asymptotic (large-R) forms. Because the ground state of HeH^+ is sought, the lowest-energy asymptotic states are used. Accordingly, our *Ansatz* for ψ_1 is

$$
\psi_1(\vec{r}_1,\vec{r}_2) = \left[\left[\frac{8}{\pi} \right]^{1/2} e^{-2r_{A2}} \right] \left[\left[\frac{1}{\pi} \right]^{1/2} e^{-r_{B1}} \right] , \tag{3.24}
$$

with a similar form for ψ_2. Applying these *Ansätze* to (3.23) gives for the ground state an equilibrium internuclear separation of $1.1a_0$ with corresponding energy minimum of -2.7973 a.u. This result compares extremely unfavorably to the numerically exact ones (see Table VII). In retrospect, this partial failure is not too surprising since that channel with the largest internal binding energy and the associated configuration likely to contribute most to the ground state, viz., $\mathrm{He} + \mathrm{H}^+$, has been neglected in (3.24). In order to include this third channel in the calculation, a third partitioning of the Hamiltonian (3.20) is required:

$$
\begin{aligned}
H_3 &= -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{2}{r_{A1}} - \frac{2}{r_{A2}} + \frac{1}{r_{12}} \,, \\
V^3 &= \frac{2}{R} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} \,.
\end{aligned}
$$

The approximate ACQM equations, enlarged to include this new channel, are now

$$
\begin{bmatrix} H_1 & V^2 & 0 \\ 0 & H_2 & V^3 \\ V^1 & 0 & H_3 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} . \tag{3.25}
$$

As with the hydrogen molecule, each channel component in (3.25) could be expanded in a complete set of functions to transform these into a linear algebraic eigenvalue problem. However, it is desirable instead to ascertain the relative accuracy that can be obtained by using only the most intuitive *Ansätze* as input to the solution of (3.25). A partial set of intuitively motivated approximate channel components is already provided by (3.24). To complete this set, a form for ψ_3 is required. Asymptotically, channel (3) represents a single proton infinitely removed from a helium atom. Thus is it reasonable in this Born-Oppenheimer model to choose ψ_3 as the He ground-state wave function. Pekeris (cf. Ref. 9) has made an essentially exact variational calculation of the helium ground state using a 1075-term expansion of the wave function. Use of such an extremely complex wave function in conjunction with the simple form of (3.24) and our already truncated equations is clearly inconsistent. We choose instead the two-parameter Eckart wave function[21]:

$$
\psi_3 \propto e^{-(\zeta_1 r_{A1} + \zeta_2 r_{A2})} + e^{-(\zeta_1 r_{A2} + \zeta_2 r_{A2})} . \tag{3.26}
$$

Considered as a variational trial function for the nonrelativistic He Hamiltonian, (3.26) yields 99% of the He ground-state energy for $\zeta_1 = 1.19$ and $\zeta_2 = 2.18$. Because of this, (3.26) should be a reasonable first approximation.

Using these approximations for ψ_1, ψ_2, and ψ_3, (3.25) can be solved for the energy E as a function of R. The results of this three-channel calculation for R_e and $E(R_e)$ are given in Table VII, where they are compared to those of the previous two-channel calculation and to the exact solution.[34] The importance of including this third channel is obvious. Indeed, since ψ_3 as chosen means that the approximate solution cannot be exact even in the limit of finite internuclear separation, this calculation is a striking example of how relatively crude but intuitive approximations can yield relatively accurate results in the ACQM formalism. It has not been necessary to use either an ACQM-derived wave function, an extremely accurate approximation, or the exact He wave function for ψ_3 to obtain good results. This example suggests that ACQM can be used in a similar manner when applied to more complex problems, i.e., this suggests that ACQM could justify an atoms-in-molecules or even a molecules-in-molecules approach.[35]

IV. DISCUSSION

At the end of the preceding section, it was suggested that ACQM might justify the atoms-in-molecules and/or molecules-in-molecules approach to molecular structure. Insofar as ground states are concerned, the $\mathrm{H}_2{}^+$, H_2, and HeH^+ calculations of this present paper and the earlier ones support this suggestion. Use of exact or approximate ground states of the separated atoms, i.e., H for $\mathrm{H}_2{}^+$, $\mathrm{H}+\mathrm{H}$ for H_2, and $\mathrm{He}+\mathrm{H}^+$ for HeH^+, has led to ground-state equilibrium separations R_e and energy minima $E_e = E(R_e)$ for $\mathrm{H}_2{}^+$, H_2, and He that are remarkably accurate given the simplicity of the approximations. In particular, if we denote the separated atom energy by $E(\infty)$, then the spectroscopic dissociation energy $D_e = E(\infty) - E_e$ for each of these molecules displays an accuracy which seems also disproportionate when compared to the ease with which one obtains these numbers using the ACQM formalism.

That one could obtain a relatively high degree of accuracy for the ground-state values of R_e and D_e using the CPA equations in the $\mathrm{H}_2{}^+$ and H_2 case was of course known prior to the present calculations. It was, however, somewhat difficult to accept the original $\mathrm{H}_2{}^+$ and H_2 results unequivocally, since first, there were only two of them, and second, the associated *ungerade* $H_2{}^+$ and triplet H_2 energy curves were unphysical for $R \rightarrow 0$. In addition, the ACQM formalism represented a relatively unknown and not well-tested methodology. The possibility that the $H_2{}^+$ and H_2 ground-state results were fortuitous was thus obvious and immediate.

There were two procedures by which one could have investigated this possibility (and presumably showed it to be unfounded). These were to apply the CPA formalism to the calculation of the ground states of more complex molecules or else to concentrate on the simpler ones and determine how convergence is achieved for them in the ACQM formalism. The study we undertook combined these, in that our main effect was concentrated on convergence questions, which we believe is the more important feature, while a minor effect went into demonstrating that the ground state of HeH^+ is quite well represented in the ACQM formalism as a linear combination of the $He + H^+$ and $He^+ + H$ ground states.

The first conclusion we wish to draw from the results reported herein is that the achievement of relatively high accuracy—much greater accuracy, for example, obtained via the corresponding Schrödinger-equation—based variational calculations—is not fortuitous: Enough calculations on molecular (and atomic[9]) ground and certain low-lying states now seem to have been carried out to establish this. Furthermore, the formalism itself has provided a relatively simple criterion—viz., the energy of the asymptotic states—for determining which channels and which bound states in them should play the most important role in initial attempts to determine an accurate approximate calculation of ground states. Most of the energy $E(R)$ obviously comes from the H_i portions of $\underline{H}$; the remainder effectively arises from the (attractive) matrix elements of V^i, the intercluster interaction. For the three cases examined here, these latter matrix elements yield between -0.06 and -0.16 a.u. additional binding energy: In ACQM this is the glue that holds the asymptotic fragments together.

That the additional energy is attractive is not altogether unexpected. Solving (3.4), e.g., for ψ_2 yields

$$E\psi_1 = H_1\psi_1 + V^2(E - H_2)^{-1}V^1\psi_1 \; . \tag{4.1}$$

The second term in (4.1) is in a form that could be described as a second-order *rearrangement* perturbation theory term. Now in Rayleigh-Schrödinger perturbation theory, we know that the effect of the second-order term is to lower the energy. The similarity in structure between this latter term and the second term in (4.1) is at least suggestive that in ACQM, one will also get a lowering of the energy, now due to the channel coupling. While this is only an analogistic plausibility argument, the simplest ACQM ground-state calculations are consistent with it, and thus lend a degree of credence to our expectation that ACQM can yield, via simple computations, a physical model of chemical bonding.[10]

Even though the preceding remarks, strictly speaking, are valid only for a few two-electron molecules, we find the results encouraging. Nevertheless, we are still forced to draw a second, much less encouraging conclusion: The basis set expansions studied in the present paper do not even hint that the extended ACQM calculations converge to the correct answers. This is, of course, a very nontrivial problem. Even though the simple ACQM calculations yield sufficiently accurate numbers to provide a physical picture of the chemical bond for $H_2{}^+$, H_2, and HeH^+, these calculations can be accepted as reliable only if the method converges.

Since the Galerkin-Petrov method does converge if a complete set of expansion states are employed,[18] there are only two reasons for the extended calculations of this paper to give no indication of convergence: either an insufficient basis has been used and/or the CPA formalism, which is based on scattering theory, cannot be used to calculate bound states.

In the first instance, the problem could be due either to properties associated with $\underline{H}^\dagger \neq \underline{H}$ or to the long-range nature of the Coulomb interaction, as in the case of the Faddeev equation approach[6,36] (or both). In the second instance, we would be facing an unexpected situation, viz., one in which a supposedly correct scattering theory involved equations for transition operators which could not be analytically continued to negative energies. This situation might arise because theorems concerning uniqueness which are valid for scattering and are believed to hold for bound states are in fact invalid in this latter case,[37] or perhaps because the spurious solution spectrum could interfere with that of the physical solutions.[38] If either of these latter alternatives are true, then all the ACQM structure calculations are fortuitous, despite the above comments to the contrary, and the CPA equations can only be used for scattering. In light of this possibility, it seemed necessary to continue our attempts to obtain a converged result. As noted in previous sections, our attempts using a locally defined basis set were successful. The method, results and implications are described in the next paper.

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