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Channel-coupling array analysis of electron correlation in $H_3{}^+$

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The three-center, two-electron molecular ion $H_3{}^+$ has been studied using the channel-coupling array theory of n-particle scattering. The aim has been to determine how well the simplest approximations to the theory can handle electron correlation in a well-studied, three-center system. Two sets of approximate calculations of the ground-state energy of $H_3{}^+$ are described. In the first, a channel-truncation approximation was used to yield a set of three coupled equations involving the three H_2+H^+ channels. The channel-component wave functions were then approximated by hydrogenic $1s$ states; both the energy and equilibrium separation were poor. For the second set, a technique was developed in which the H_2 cluster in each of the preceding H_2+H^+ channels was subpartitioned into an $H + H$ subchannel. The use of hydrogenic $1s$ states for the $H + H$ subchannel components yielded much more accurate results: $E(R=1.67a_0)=-1.307$ a.u., compared to a valence-bond calculation with $1s$ states $E(R=1.66a_0)=-1.298$ a.u. As in previous calculations of this type, the results were obtained with relative computational ease.

I. INTRODUCTION

In this paper we study the effect of electron-electron correlation in the three-center molecular ion $H_3{}^+$ using the channel-coupling array theory approach to molecular structure and very simple approximations to the wave-function components of this theory. We show that within this type of approach, the treatment of correlation can be dramatically improved by using the channel-coupling array method to subpartition the (two-electron) H_2 subsystem that appears in the partitions of the full $H_3{}^+$ system. The background underlying this study and the motivation for undertaking it are described in the remainder of this section.

The channel-coupling array (CCA) theory represents one framework for imposing the boundary conditions needed to ensure a unique solution to the Schrödinger equation describing n-particle collisions, $n>2$. This is accomplished by means of a set of coupled equations for wave-function components; the components asymptotically yield matrix elements describing transitions among continuum states. These same coupled equations may also be solved for the bound states of the n-particle system, and a number of such calculations have been carried out for some two-center molecules containing one or two electrons.[1-10]

Most of the bound state CCA calculations have been approximate. Now that we understand how to obtain physically well-behaved *ungerade* energy curves,[4,5,8] most of these CCA calculations may be characterized as having yielded approximate energy curves that are much more accurate than might have been expected given the crudity of the approximated channel components. Indeed, for the case of ground states, use of uncorrelated, two-electron, approximate wave-function components has led to approximate energies which include substantial amounts of the correlation energy. More generally, most of the CCA results can be contrasted with their Schrödinger counterparts as follows. Let $\tilde{\psi}_i$ denote the approximation to the exact component ψ_i for channel i. The approximate Schrödinger solution $\tilde{\Psi}$ is related to the approximate components $\tilde{\psi}_i$ via[2] $\tilde{\Psi}=\sum\tilde{\psi}_i$, where i is summed over the relevant channel labels. Then, if the components $\tilde{\psi}_i$ are formed from one or a few low-lying states corresponding to a separated atom picture, the resulting CCA molecular energy is generally much more accurate than is the energy obtained by using $\tilde{\Psi}=\sum\tilde{\psi}_i$ in a Rayleigh-Ritz variational calculation.[1-3,6,9] (Also, the computational effort required to determine the CCA energy curve is generally much less than required in a variational calculation.) As noted, an exception to this situation had been the unphysical nature of the CCA energy curves for the *ungerade* states of $H_2{}^+$ and H_2, but these have been recently eliminated[5,8] through imposition of boundary conditions that had not been previously applied.

Let us recall some of these computations. In the crudest approximations, the component $\tilde{\psi}_i$ was simply an uncorrelated product of states for each of the systems forming the separated atom picture. For example, $H_2{}^+$ was represented by components describing a noninteracting H and H^+ pair,[1,2] while H_2 (in the channel-truncation approximation) was represented by components describing a noninteracting pair of H atoms.[3] In both of these examples only one-electron states were used to form the approximate channel components. This was no longer possible in the case of HeH^+, for which the inclusion of the channel $He+H^+$ was found to be essential.[6] The component for the He cluster in this channel was approximated by a simple (correlated) Eckart wave function;[11] the resulting CCA dissociation energy was quite accurate even though no excited He states were included in the calculation.[6]

While this latter result suggests that correlation within a cluster can be successfully treated in a CCA approach, a more stringent test will be to determine how well the method describes correlation in a three-center, two-electron cluster. With this goal in mind, we chose to study H_3^+. In the channel-truncation approximation, only the $H_2 + H^+$ channels are retained, and the effect of electron correlation in the H_2 cluster can be studied directly.

Although there is no experimental data available on the ground state of H_3^+, many theoretical values for the energy of the equilibrium configuration are available[12–21] against which the CCA results could be compared. These are listed in Table I. The aim of the present investigation has been to determine the accuracy of the approximate CCA energy curve obtained using the simplest *Ansatz* for H_3^+. This is consistent with the aim and philosophy of previous CCA calculations. These latter have shown that, within the CCA framework, the use of very simple *Ansätze* for the ground-state wave-function components for H_2^+, H_2, and HeH^+ can produce sufficiently accurate energy curves that a physical picture of the structure or of the chemical bond emerges.[2,3,9] We initiated the current study of H_3^+ anticipating that our calculations would yield a similar conclusion.

There are two other features that characterize the current study. One is the relative ease in performing the CCA computations as compared to the variational ones: as we note at the end of Sec. III, the number of integrals evaluated in the CCA calculation was about 2 orders of magnitude less than were evaluated by Christofferson.[13] The second point is more fundamental: we present a method for treating electron correlation in this system that does not employ correlated, two-electron channel components; this method of subpartitioning is described in Sec. III.

TABLE I. Theoretical values for the energy of the equilibrium configuration. Acronym definitions are as follows: VB, valence bond; NO, natural orbitals; GTO, Gaussian-type orbitals; STO, Slater-type orbitals; CI, configuration interaction; MO, molecular orbitals; FGTO, floating GTO; GL, Gaussian lobes; SCF, self-consistent field.

Ref.	Method	Energy (a.u.)	R (a_0)
	Comparison of simple calculations for H_3^+		
16	VB STO $1s$ (cov.)	-1.2924	1.66
13	VB STO $1s$ (cov. and ionic)	-1.2979	1.66
	CCA STO $1s$ (current work)	-1.3066	1.67
	Comparison of extensive calculations for H_3^+		
14	SCF MO GTO	-1.2988	1.62
15	SCF MO STO	-1.2863	1.6229
16	SCF MO FGTO	-1.2999	1.6405
13	CI MO STO (12 configurations)	-1.3326	1.6575
17	CI STO (100 configurations)	-1.3405	1.650
16	CI MO FGTO	-1.3376	1.6504
18	CI GL (48 configurations)	-1.3405	1.6406
21	NO GL	-1.3359	1.66
19	Correlated Gaussian	-1.3434	1.650
20	Random walk	-1.3439	1.650

II. CCA EQUATIONS FOR H_3^+

In the CCA theory the particles of the system are grouped into clusters, where a cluster can consist either of a bound system of particles or of a single particle. Each partitioning of the system into clusters is denoted a channel, which corresponds to a separated atom picture of the system. In order to obtain unique solutions to the CCA equations in the case of scattering, it is sufficient to include only the two-cluster channels.[22] By means of analytic continuation to negative energies, a similar result is inferred to hold in the bound-state case.[2,9] This has been verified for H_2^+ by Ford and Levin.[7]

H_3^+ can be partitioned into nine two-cluster channels, three of the type $H_2 + H^+$ and six of the type $H_2^+ + H$. In a truncated-channel approximation, the channels whose asymptotic states require the minimum dissociation energy are retained. The ground-state energy of the hydrogen molecule is -1.174 a.u. compared to -1.103 a.u. for the combination of the hydrogen molecular ion and hydrogen atom. Therefore, the present calculation employs only the three $H_2 + H^+$ channels.

If the three protons are labeled a, b, and c, and the two electrons 1 and 2, then the three retained channels are denoted

$$\begin{aligned} &\text{channel } a:\ (1,2,c,b)+a\ ,\\ &\text{channel } b:\ (1,2,a,c)+b\ ,\\ &\text{channel } c:\ (1,2,a,b)+c\ . \end{aligned} \tag{2.1}$$

The channel Hamiltonian H_α consists of the kinetic energy of the electrons plus all interactions internal to the clusters of channel α. For $\alpha = a$, the channel Hamiltonian H_a is

$$H_a = H_0 - 1/r_{c1} - 1/r_{b2} - 1/r_{c2} - 1/r_{b1} + 1/R_{bc} + 1/r_{12}\ , \tag{2.2}$$

where H_0 is the kinetic-energy operator and, e.g., r_{b1} is the distance between proton b and electron 1. Similarly, the channel interaction V^a contains all of the intercluster interactions in channel a:

$$V^a = -1/r_{a1} - 1/r_{a2} + 1/R_{ac} + 1/R_{ab}\ . \tag{2.3}$$

Analogous relations hold for $\alpha = b$ and $\alpha = c$.

For any given channel, the sum of the channel Hamiltonian and channel interaction is the Schrödinger Hamiltonian; the Schrödinger wave function Ψ is equal to the sum of the two-cluster channel components ψ_α:

$$H = H_\alpha + V^\alpha \quad \text{for all } \alpha\ , \tag{2.4}$$

$$\Psi = \sum_\alpha \psi_\alpha\ . \tag{2.5}$$

In the present case of a $9\times 9 \rightarrow 3\times 3$ truncation, the sum over α includes only the three $H_2 + H^+$ channels retained in the channel-truncation approximation. These three components obey the 3×3 CCA matrix equation[2]

$$\begin{bmatrix} H_a-E & V^b & 0 \\ 0 & H_b-E & V^c \\ V^a & 0 & H_c-E \end{bmatrix} \begin{bmatrix} \psi_a \\ \psi_b \\ \psi_c \end{bmatrix} = 0 \; . \tag{2.6}$$

On projecting (2.6) to the left onto a row vector $[\psi_a,\psi_b,\psi_c]$, the three coupled equations can be solved for the (channel-truncated) energy E.

The operators H_α and V^α $(\alpha=a,b,c)$ obey the symmetry relations

$$\begin{aligned} H_b &= P_{abc}^{\dagger} H_a P_{abc} \; , \quad V^b = P_{abc}^{\dagger} V^a P_{abc} \; , \\ H_c &= P_{abc}^{\dagger} H_b P_{abc} \; , \quad V^c = P_{abc}^{\dagger} V^b P_{abc} \; , \\ H_a &= P_{abc}^{\dagger} H_c P_{abc} \; , \quad V^a = P_{abc}^{\dagger} V^c P_{abc} \; , \end{aligned} \tag{2.7}$$

where P_{abc} is the cyclic permutation operator that replaces a with b, b with c, and c with a. Using the unitarity of the permutation operator, viz., $P_{abc}^{\dagger} P_{abc}=1$, and Eqs. (2.6) and (2.7), it can be shown that the ground-state (singlet, *gerade)* channel components defined by (2.6) obey the symmetry relations

$$\begin{aligned} \psi_b &= P_{abc}\psi_a \; , \\ \psi_c &= P_{abc}\psi_b \; , \\ \psi_a &= P_{abc}\psi_c \; . \end{aligned} \tag{2.8}$$

Hence, if Eq. (2.6) is multiplied from the left by a row vector which satisfies (2.8), it follows that

$$\langle \psi_a \,|\, H_a \,|\, \psi_a \rangle = \langle \psi_b \,|\, H_b \,|\, \psi_b \rangle = \langle \psi_c \,|\, H_c \,|\, \psi_c \rangle \tag{2.9a}$$

and

$$\langle \psi_a \,|\, V^b \,|\, \psi_b \rangle = \langle \psi_b \,|\, V^c \,|\, \psi_c \rangle = \langle \psi_c \,|\, V^a \,|\, \psi_a \rangle \; . \tag{2.9b}$$

Thus, in the channel-truncation approximation, the three coupled CCA equations (2.6) collapse to a single expression for the energy:

$$E\langle \psi_a \,|\, \psi_a \rangle = \langle \psi_a \,|\, H_a \,|\, \psi_a \rangle + \langle \psi_a \,|\, V^b \,|\, \psi_b \rangle \; . \tag{2.10}$$

If the components $[\psi_a,\psi_b,\psi_c]$ which solve Eq. (2.10) exactly are replaced by approximate ones $[\tilde{\psi}_a,\tilde{\psi}_b,\tilde{\psi}_c]$ that obey the symmetry relations (2.8), then an approximate energy $\tilde{E}$ can be determined from

$$\tilde{E}\langle \tilde{\psi}_a \,|\, \tilde{\psi}_a \rangle = \langle \tilde{\psi}_a \,|\, H_a \,|\, \tilde{\psi}_a \rangle + \langle \tilde{\psi}_a \,|\, V^b \,|\, \tilde{\psi}_b \rangle \; . \tag{2.11}$$

In carrying out the computations which employed (2.11), the equilateral triangle was assumed to be the equilibrium configuration. Although not confirmed experimentally the equilibrium configuration has been established by previous work on H_3^+.[12-21] Hence, $\tilde{E}$ was assumed to depend on only one length R, where $R=R_{ab}=R_{bc}=R_{ac}$. Since the goal was to obtain a relatively accurate approximate energy $\tilde{E}(R)$ using crude approximate wave-function components, the H_3^+ channel components used initially were constructed from simple hydrogenic states, viz.,

$$\tilde{\psi}_a = \exp(-r_{b1})\exp(-r_{c2}) + \exp(-r_{b2})\exp(-r_{c1}) \; . \tag{2.12}$$

Although the resulting energy was only slightly worse than a valence-bond calculation using $1s$ states,[12] the equilibrium separation was off by over 30% (see Fig. 1). In an attempt to improve this result, a scaling factor was next introduced into the hydrogenic states of (2.12) and the energy was minimized with respect to this effective nuclear charge. The energy was lowered by less than 1%, although the equilibrium separation was improved by 10%. (Since the minmax principle does not apply to the non-Hermitian CCA equations,[2,23] free parameters in the channel components must be used with discretion.) Use of very simple approximate components in Eq. (2.11) is thus seen not to yield very accurate results. This is evidently connected with the use of uncorrelated wave functions to describe the H_2 subsystem in each channel. An obvious means for attempting to improve these results is to replace $\tilde{\psi}_a$ of (2.12) by a wave function which more accurately describes H_2.

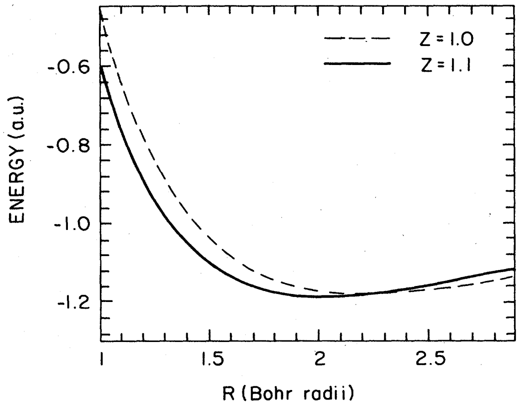

FIG. 1. Simplest CCA ground-state energy for H_3^+.

Although correlation was introduced straightforwardly in the two-electron cluster He in the CCA calculation on HeH^+, constructing a component to describe the electron correlation in a two-center cluster is considerably more difficult. Furthermore, such a replacement is counter to the spirit of this study, as noted above. Rather than attempt to improve $\tilde{E}(R)$ simply by altering $[\tilde{\psi}_a,\tilde{\psi}_b,\tilde{\psi}_c]$, the CCA method was reapplied, this time to Eq. (2.6), as described in Sec. III.

III. SUBPARTITIONED CCA EQUATIONS FOR H_3^+

The calculations just summarized show that use of a channel component which ignores the effect of electron-electron interaction within the cluster generates a rather poor energy curve. Constructing channel components from Hylleraas functions, which depend explicitly on the interelectronic distance, could lower the energy several percent. However, the resultant three-center integrals would greatly complicate the evaluation of $\tilde{E}$, and the main attraction of the CCA approach so far has been the comparative ease with which it produces a relatively accurate energy. In an attempt to avoid increasing the complexity of the channel components, an algorithm was devised for subpartitioning the H_2 clusters into their simpler constituents, i.e., for applying the CCA procedure to the individual clusters. While the simplicity of the components is retained, there is a concomitant increase in operator complexity.[23]

The procedure by which the H_2 cluster in each of the original channels is subpartitioned into an H + H subchannel is identical to the CCA (channel-truncated) treatment of the H_2 molecule.[3] For example, the H_2 cluster $(b,c,1,2)$ of channel a is subpartitioned in the following manner:

$$\text{channel } a \rightarrow \begin{cases} \text{channel } a\,1\text{:} & [(b,1)+(c,2)]+a\ , \\ \text{channel } a\,2\text{:} & [(b,2)+(c,1)]+a\ . \end{cases} \tag{3.1}$$

The operators for subchannel a 1 are

$$\begin{aligned} H_{a1} &= H_0 - 1/r_{b1} - 1/r_{c2}\ , \\ V^{a1} &= -1/r_{b2} - 1/r_{c1} + 1/R + 1/r_{12}\ , \end{aligned} \tag{3.2}$$

with corresponding expressions for H_{a2} and V^{a2}. The effect of this subpartitioning is that the electron-electron interaction has been removed from the channel Hamiltonian and incorporated into the external subchannel potential operator.

In the 9×9→3×3 truncation, the original channel operators and components are related to the new subchannel operators and components by

$$H_a = H_{ai} + V^{ai}\ , \quad i=1,2 \tag{3.3}$$

$$\psi_a = \sum_i \psi_{ai}\ . \tag{3.4}$$

Substituting Eqs. (3.3) and (3.4) into (2.4) and (2.5) gives the Schrödinger Hamiltonian and wave function in terms of the subchannel operators and components:

$$H = H_{ai} + V^{ai} + V^a, \quad a=a,b,c, \quad i=1,2 \tag{3.5}$$

$$\Psi = \sum_a \sum_i \psi_{a,i}\ . \tag{3.6}$$

Although the structure of the subchannel components can be simpler than that of the channel components, the equations they obey are more complex, since the original channel Hamiltonian H_a and external channel potential V^a are replaced by 2×2 matrices:

$$H_a \rightarrow \begin{bmatrix} H_{a1} & V^{a2} \\ V^{a1} & H_{a2} \end{bmatrix}, \tag{3.7}$$

$$V^a \rightarrow \begin{bmatrix} V^a & V^a \\ V^a & V^a \end{bmatrix}. \tag{3.8}$$

Similarly, the channel component ψ_a is replaced by a column vector whose components are ψ_{a1} and ψ_{a2}. These new subchannel components are the solution of the 6×6 matrix equation obtained by substituting Eqs. (3.7) and (3.8) into the 3×3 CCA matrix equation (2.6):

$$\begin{bmatrix} H_{a1}-E & V^{a2} & V^b & V^b & 0 & 0 \\ V^{a1} & H_{a2}-E & V^b & V^b & 0 & 0 \\ 0 & 0 & H_{b1}-E & V^{b2} & V^c & V^c \\ 0 & 0 & V^{b1} & H_{b2}-E & V^c & V^c \\ V^a & V^a & 0 & 0 & H_{c1}-E & V^{c2} \\ V^a & V^a & 0 & 0 & V^{c1} & H_{c2}-E \end{bmatrix} \begin{bmatrix} \psi_{a1} \\ \psi_{a2} \\ \psi_{b1} \\ \psi_{b2} \\ \psi_{c1} \\ \psi_{c2} \end{bmatrix} = 0\ . \tag{3.9}$$

Although the subpartitioning increases the order of the CCA operator matrix, the symmetry of the new equations again allows a significant simplification. The ultimate symmetry of the resulting equations is dependent on the particular choice of ordering labels in the channels.

The symmetry of the subchannel operators is defined with the cyclic permutation operator P_{abc} and the electron exchange operator P_{12}:

$$\begin{aligned} P_{abc}^{\dagger} H_{a1} P_{abc} &= H_{b1}\ , \quad P_{12}^{\dagger} H_{a1} P_{12} = H_{a2}\ , \\ P_{abc}^{\dagger} V^{a1} P_{abc} &= V^{b1}\ , \quad P_{12}^{\dagger} V^{a1} P_{12} = V^{a2}\ , \\ P_{abc}^{\dagger} V^{a} P_{abc} &= V^{b}\ , \quad P_{12}^{\dagger} V^{a} P_{12} = V^{a}\ , \end{aligned} \tag{3.10}$$

and similarly for the other subchannels. These relations and the unitarity of P_{abc} and P_{12} can now be used to determine the symmetry of the subchannel components for the ground state:

$$P_{abc}\psi_{a1} = \psi_{b1}, \quad P_{12}\psi_{a1} = \psi_{a2}\ . \tag{3.11}$$

It is trivial to show, in analogy to (2.9a) and (2.9b), that

$$\begin{aligned} \langle \psi_{\alpha i} | H_{\alpha i} | \psi_{\alpha i} \rangle &= \langle \psi_{\beta j} | H_{\beta j} | \psi_{\beta j} \rangle\ , \\ \langle \psi_{\alpha i} | V^{\alpha i} | \psi_{\alpha j} \rangle &= \langle \psi_{\beta j} | V^{\beta j} | \psi_{\beta i} \rangle\ , \\ \langle \psi_{\alpha i} | V^{\beta} | \psi_{\beta i} \rangle &= \langle \psi_{\alpha i} | V^{\beta} | \psi_{\beta j} \rangle\ , \\ \langle \psi_{\alpha i} | V^{\beta} | \psi_{\beta i} \rangle &= \langle \psi_{\beta i} | V^{\delta} | \psi_{\delta i} \rangle\ , \end{aligned} \tag{3.12}$$

where α,β,δ is cyclic in a,b,c and i,j takes on the values 1 and 2. Equations (3.11) and (3.12) reduce the 6×6 set, Eq. (3.9), to a single equation for the (channel-truncated) energy:

$$\begin{aligned} E(R)\langle \psi_{a1} | \psi_{a1} \rangle = \langle \psi_{a1} | H_{a1} | \psi_{a1} \rangle + \langle \psi_{a1} | V^{a2} | \psi_{a2} \rangle \\ + \langle \psi_{a1} | V^{b} | \psi_{b1} \rangle + \langle \psi_{a1} | V^{b} | \psi_{b2} \rangle\ . \end{aligned} \tag{3.13}$$

Replacement of the subcomponents ψ_{ai} in (3.13) by approximate ones $\tilde{\psi}_{ai}$, yields an approximate energy $\tilde{E}(R)$.

Because the subchannels of the H_2 cluster of $H_3{}^+$ are identical to the channels that were retained in the original

H_2 ground-state calculation,[3] the same simple molecular orbital (MO) states that produced an accurate H_2 ground-state energy curve in Ref. 3 were chosen for the approximate subchannel components:

$$\tilde{\psi}_{a1}=\exp(-r_{b1})\exp(-r_{c2}) ,$$
$$\tilde{\psi}_{a2}=\exp(-r_{b2})\exp(-r_{c1}) . \quad (3.14)$$

Note that $\tilde{\psi}_{a1}+\tilde{\psi}_{a2}$ yields the approximate channel component $\tilde{\psi}_a$ of Eq. (2.12).

The curve generated by Eqs. (3.13) and (3.14) improved both the energy minimum and equilibrium separation: $\tilde{E}(R=1.92a_0)=-1.286$ a.u. Although these results are improvements over the calculations described in Sec. II, the error in the equilibrium separation is still greater than 15%. While subpartitioning seems to be a move in the right direction, using the same channel components as were employed in the H_2 molecule calculation is only partially successful. This can be attributed to the presence of the third proton in $H_3{}^+$, whose distance from each of the two protons in the H_2 cluster is equal to the interproton separation in the cluster. Even in the CCA approach, this "spectator" proton should distort the purely hydrogenic states of the *Ansätze* of (3.14). To take account of this third proton, an effective-charge scale factor Z was introduced into the hydrogenic states. Minimizing the energy with respect to Z results in a more dramatic improvement in $\tilde{E}(R)$ than observed in the previous calculation without the subpartitioning of the channels. With the scaling factor of $Z=1.14$, the CCA minimum energy is $\tilde{E}(R=1.67a_0)=-1.307$ a.u. (Fig. 2).

A comparison of the CCA results and other calculations on $H_3{}^+$ is shown in Table I. As in the cases of $H_2{}^+$, H_2, and HeH^+, the CCA method has again produced a better approximate energy than the variational result when the total approximate wave function is constructed from simple $1s$ states. Indeed, configuration-interaction (CI) calculations using hydrogenic states yield an energy comparable to the CCA results only when contributions from $1s$, $2s$, and $2p$ were included. The CI calculations required the evaluation of hundreds of integrals, including many three-center ones.[13] In contrast, the CCA method involves the evaluation of just five integrals, only one of which was three-center. Since most multicenter integrations must be performed numerically, the CCA method offers a considerable savings in computer time and still yields a reasonable approximate ground-state energy for $H_3{}^+$. The resulting approximate Schrödinger wave function is simple and the energy is accurate enough that a physical picture of $H_3{}^+$ emerges from this analysis: it behaves like a system of one proton and two hydrogen atoms whose electrons experience a modified charge.

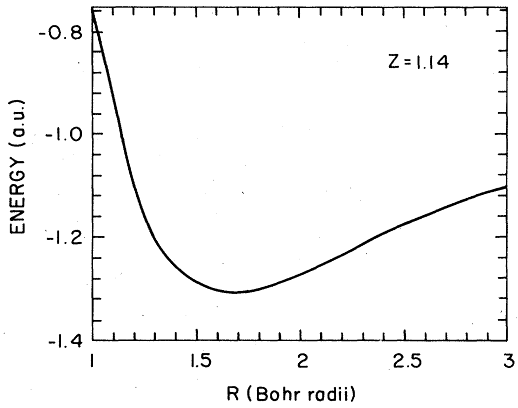

FIG. 2. Subpartitioned CCA ground-state energy for $H_3{}^+$.

IV. DISCUSSION

The method of subpartitioning the two-electron cluster in $H_3{}^+$ has been successful in that it led to a simple treatment of electron correlation in the H_2 cluster and a relatively accurate energy curve was produced with minimal computation. However, there may be limitations to the applicability of this method to other multicenter, multielectron systems. The subpartitioning of clusters increases the operator complexity considerably. In the present case, the symmetry of the subchannels allowed a remarkable reduction in complexity. For larger molecules, subsequent partitioning of subclusters could result in very large matrices, while a lack of symmetry could prevent a substantial reduction of the matrix equations. In such cases, the energy could still be obtained in practice, although the computer effort required to evaluate the matrix elements probably would no longer be significantly less than that required in a standard (CI) calculation. Another problem may occur with a cluster containing more electrons than protons, e.g., an $H_2{}^-$ cluster. Among the subpartitionings of such a cluster would be an isolated electron. Although the CCA method has successfully handled an isolated electron in the multielectron atom,[9] the extension to the molecular case is not straightforward. Therefore, the subpartitioning of negative ionic channels may not be practical, although this is a matter requiring investigation. Both of these problems could limit the use of the subpartition method in larger molecules. Nevertheless, a significant step has been taken in using the CCA approach to understand the ground-state structure of complex systems.

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