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Complex potential-energy function for the $^2\Sigma_u^+$ shape resonance state of H_2^- at the self-consistent-field level

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The complex potential-energy function for nuclear motion in the Born-Oppenheimer approximation for the lowest $^2\Sigma_u^+$ resonance state of H_2^- has been calculated using the complex self-consistent-field (CSCF) method which treats the incident and target electrons equivalently. There is substantial disagreement among various determinations of the complex potential function for the broad $^2\Sigma_u^+$ resonance. The CSCF results agree best with the potential used by Bardsley and Wadehra [Phys. Rev. Lett. 41, 1795 (1978)] to compute dissociative attachment cross sections. The calculated width of the resonance as a function of internuclear distance is in excellent agreement with the form used by Bardsley and Wadehra while the real part of the CSCF potential agrees less well with their function. It is suggested that correlation effects are important in determining the position of the resonance and in determining the width at least near the internuclear distance at which the resonance becomes a bound state.

I. INTRODUCTION

Resonances in electron-molecule scattering can enhance the probabilities of vibrational excitation and dissociative attachment and, in some cases, dominate the cross sections for these processes. For example, the prominant $^2\Pi_g$ resonance occurring at about 2.5 eV in e-N_2 scattering is a well studied case of resonance enhancement of vibrational excitation, and low-energy dissociative attachment in e-H_2 scattering which proceeds through the broad $^2\Sigma_u^+$ shape resonance is an example of resonance enhancement of dissociative attachment. The autoionizing states of molecules through which Penning ionization proceeds are also resonances (in electron scattering from the molecular ion), and the lifetime of such states is an important factor determining the Penning ionization cross section. In spite of the central role resonances can play in collision processes there have been relatively few *ab initio* calculations of the energies and lifetimes of molecular resonances.[1-5]

The simplest information from which the resonant contribution to vibrational excitation can be approximately calculated is that required by the "boomerang model" of Birtwistle and Herzenberg[6] and Dube and Herzenberg[7] or by the "energy modified adiabatic approximation" of Nesbet,[8] namely, the complex potential-energy surface for nuclear motion in the resonance state. For a diatomic molecule this potential $E_{\text{res}}(R)$ depends on the internuclear distance R and is generally denoted

$$E_{\text{res}}(R)=E_R(R)-i\Gamma(R)/2\ , \tag{1}$$

where $E_R(R)$ is the (real-valued) position of the resonance and $\Gamma(R)$ is the width. More elaborate theories[9] require a nonlocal complex potential in place of the local one in Eq. (1).

Dube and Herzenberg[7] point out that to reproduce the experimental vibrational excitation cross section in a case for which the boomerang model is applicable it may be necessary to have a representation of $E_{\text{res}}(R)$ accurate to about $10^{-2}\ a_0$. That is to say that, because the vibrational excitation cross section is sensitive to details of the potential surface on the scale of the wavelength for nuclear motion, it is necessary to locate critical features such as classical turning points to within less than one wavelength. Certainly if such accuracy is to be obtained in an *ab initio* calculation—even for the simplest case—it will be necessary to have methods for computing the complex energies of resonance states which make those calculations no more difficult than the calculation of the real energies of bound states. In this paper we present the calculation of the complex potential-energy curve for the lowest-energy shape resonance in electron-H_2 scattering, the $^2\Sigma_u^+$ state, in which all three electrons are treated on a precisely equal footing in a self-consistent-field (SCF) calculation on H_2^-. As we have shown in previous publications,[3,10,11] the SCF equations have solutions with complex energies for shape resonance states, and these solutions can be found using complex basis functions in the complex self-consistent-field (CSCF) method. These calculations include a substantial portion of the response of the target because the target orbitals (only the $1\sigma_g$ in this case) are calculated in the field of the incident electron and thus can "relax" in its presence. A previous calculation on the $^2\Pi_g$ resonance state of N_2^- suggests that for closed-shell molecular targets the CSCF approximation can provide accurate results, particularly for the width of the resonance.[3]

If the accurate *ab initio* calculation of molecular resonance parameters is to become commonplace it will be necessary to develop methods which address this problem with all the power and flexibility of conventional bound-state ("quantum chemistry") calculations. The effects of electron correlation on the width, for example, may be subtle and, since the correlation problem is a formidable one even in bound-state calculations, we cannot afford to introduce many additional computational difficulties into the molecular resonance problem. The CSCF calculations presented here provide a logical starting point for configuration interaction (CI) studies of the $^2\Sigma_u^+$ resonance in e-H_2 scattering. Most of the computational problems associated with complex basis function calculations are associated with the calculation of one- and two-electron integrals and have been overcome effectively at this point, so the additional effort required to perform CI calculations on this small system is not major.

The $^2\Sigma_u^+$ state of H_2^- dissociates to $H + H^-$ and therefore, since H^- is a bound anion, the resonance state of H_2^- must become a bound state as R increases. In Sec. IV we will present the CSCF description of this change from resonance to bound state. Part of the motivation for these calculations was to determine if the solution of the CSCF equations is a continuous function of R as the change from resonance to bound state occurs, and to develop procedures for finding solutions in the transition region.

The outline of this paper is as follows. In Sec. II we present a brief description of the CSCF method. In Sec. III we discuss some of the computational details including the basis sets employed and the location of complex stationary points. Section IV presents our numerical results and compares them with empirical and theoretical results of other workers, including the recent work of Wadehra and Bardsley.[12] Finally, in Sec. V we discuss further applications and extensions of the CSCF method for molecular systems.

II. THE COMPLEX SCF METHOD

Since the CSCF approach has been described elsewhere[10,11] in detail we will limit the discussion here to a brief summary of the theory and a few essential computational details. The original development[10] of the CSCF method was motivated by the use of dilatation analyticity in atomic resonance calculations.[13,14] The idea was based on the fact that the Schrödinger equation for an atomic system in which the coordinates of all the electrons have been scaled according to $\vec{r} \rightarrow \vec{r}e^{i\gamma}$ has a well-defined, discrete solution at complex resonance energies. Furthermore, the wave function corresponding to such a complex energy solution is square integrable. Therefore one should be able to construct the Hartree-Fock approximation to these discrete resonance states. For the case of a shape resonance, for which a one-configuration trial function is adequate, this is true at least in principle, and for Feshbach resonances we can find SCF approximations to the resonance wave functions if we employ a trial wave function consisting of at least two configurations.[10] In either case the most important point is that we are locating the resonance pole of the S matrix directly in the SCF or Hartree-Fock approximation.

However, it has become increasingly clear since the original CSCF calculations were performed that there is a more general way to think about this problem—one which suggests far more efficient computational procedures as well. Instead of beginning with the Schrödinger equation for the complex-scaled Hamiltonian $H(\{\vec{r}_i e^{i\gamma}\})$ one can begin with a generalized variational expression, which makes use of the original, real-valued Hamiltonian, but in which complex variations in the trial wave function are allowed. In other words, the complex resonance energies are the complex stationary points of a suitably chosen functional.[10,11,15] An important point here is that the dual space—the left hand side of the matrix elements appearing in our functional—is not the complex conjugate of the direct space. The equivalence of this approach to the complex-scaling method has been discussed in the context of numerical calculations previously,[10,15] and various related mathematical points concerning molecular applications[16,17] and connection with the virial theorem[18] have also been discussed in the literature.

The complex variational approach to SCF and CI calculations is known in its various manifestations as the "method of complex basis functions". Without this approach it is extremely difficult, if not impossible, to perform complex calculations on molecular systems to locate electron scattering resonances in the Born-Oppenheimer approximation.

To obtain the appropriate working equations for CSCF calculations on molecules we begin with an open-shell energy expression (expectation value of the real-valued Born-Oppenheimer Hamiltonian) like that suggested by Roothaan.[19] We will write this expression in terms of the spatial orbitals $\phi_{i\lambda\alpha}$, which will be the solutions of the CSCF equations. The subscript i is the shell index, λ labels the irreducible representation, and α distinguishes members of the irreducible representation λ. The energy expression is

$$E_{\rm CSCF}=\sum_{i\lambda} N_{i\lambda}h_{ii}^{\lambda}+\tfrac{1}{2}\sum_{i\lambda j\mu} N_{i\lambda}N_{j\mu}(a_{i\lambda j\mu}J_{i\lambda j\mu}-\tfrac{1}{2}b_{i\lambda j\mu}K_{i\lambda j\mu}) , \tag{2}$$

where $N_{i\lambda}$ is the occupation of the ith shell of λ symmetry and $a_{i\lambda j\mu}$ and $b_{i\lambda j\mu}$ are coupling coefficients. This energy expression is different from the usual bound-state expression only in the definition of the matrix elements. If d_λ and d_μ denote the degeneracy of symmetries λ and μ, the one-electron, Coulomb, and exchange matrix elements are defined *without complex conjugation* as follows:

$$h_{ii}^{\lambda}=d_{\lambda}^{-1}\sum\int \phi_{i\lambda\alpha}(r)h\phi_{i\lambda\alpha}(r)d^3r , \tag{3a}$$

$$J_{i\lambda j\mu}=(d_\lambda d_\mu)^{-1}\sum_{\alpha,\beta}\int\int \phi_{i\lambda\alpha}(r_1)\phi_{j\mu\beta}(r_2)r_{12}^{-1}\phi_{i\lambda\alpha}(r_1)\phi_{j\mu\beta}(r_2)d^3r_1d^3r_2 , \tag{3b}$$

$$K_{i\lambda j\mu}=(d_\lambda d_\mu)^{-1}\sum_{\alpha,\beta}\int\int \phi_{i\lambda\alpha}(r_1)\phi_{j\mu\beta}(r_2)r_{12}^{-1}\phi_{j\mu\beta}(r_1)\phi_{i\lambda\alpha}(r_2)d^3r_1d^3r_2 . \tag{3c}$$

To obtain an appropriate variational functional we must add a set of Lagrange multiplier terms to the energy expression in Eq. (2) to constrain the orbitals to remain orthogonal to one another. The variational functional I is then

$$I=E_{\rm CSCF}-\sum_{ij\lambda\alpha}\epsilon_{ij}^{\lambda}d_{\lambda}^{-1}\int \phi_{i\lambda\alpha}(r)\phi_{j\lambda\alpha}(r)d^3r , \tag{4}$$

where ϵ_{ij}^{λ} is the complex symmetric matrix of Lagrange multipliers. The derivation of the working SCF equations proceeds from this point onward in the same manner as in the usual bound-state case except that we allow arbitrary complex variations in the orbitals $\phi_{i\lambda\alpha}$.

Expanding the CSCF orbitals in a discrete basis produces matrix equations precisely analogous to those of bound-state SCF calculations but with matrix elements over basis functions defined without complex conjugation as in Eq. (3). Choosing the functional as we did in Eq. (4) leads to complex symmetric Fock matrices. Some numerical detail of the calculations will be discussed in the following section. We will note here, however, that all schemes for reaching convergence in a real-valued SCF calculation are not necessarily equally successful in the complex SCF case. We have no clear indication that, for example, "one-Hamiltonian" methods such as that of Davidson and Stenkamp[20] are superior to "two-Hamiltonian" approaches such as that of Roothaan.[19] However, it is very clear from our experience that in the two-Hamiltonian approach one must choose the open-shell coupling coefficients [$a_{i\lambda i\lambda}$ and $b_{i\lambda i\lambda}$ in Eq. (2)] such that the (open-shell) orbital occupied by the incident electron does not experience a potential due to itself. Although such potential terms in the open-shell Fock matrix have no effect at convergence, we find they ensure that convergence to a complex resonance state is difficult to achieve.

III. COMPUTATIONAL PROCEDURES

The first and most important step in the implementation of the CSCF method is to choose an appropriate basis in which to expand the orbitals $\phi_{i\lambda\alpha}$, i.e., to choose the space in which complex variations will be carried out. Experience in calculations on atomic shape resonances[10,11] has shown that it is sufficient to use complex basis functions only for the orbital which describes the scattered electron. In the case of the H_2^- $^2\Sigma_u^+$ shape resonance that orbital is the $k\sigma_u$ orbital of our

$1\sigma_g{}^2\, k\sigma_u$ trial function. In the first CSCF calculation on a molecule[3] it was found that it is sufficient to employ complex basis functions only for the diffuse part of the basis. In our calculations those complex functions are Gaussians of the form

$$\chi_i(\vec{r})=N(\alpha\theta^{-2})(z-A_z)e^{-\alpha_i\theta^{-2}(\vec{r}-\vec{A})^2}\ , \qquad (5)$$

where $\vec{A}$ is the vector of coordinates of the center of the function, $N(\alpha\theta^{-2})$ is the normalization constant, and $\theta=e^{i\gamma}$ is a complex-scaling parameter which all of the complex Gaussians in a given calculation have in common. The basis used here is thus a combination of real Gaussians for the target orbitals and real and complex Gaussians for the continuum orbital. More generally speaking, our prescription is to include diffuse complex Gaussians only in the symmetry λ of the continuum orbital, so that if there are target orbitals of the same symmetry they will pick up small contributions from the complex functions. Of course all of the coefficients in the expansion of target and continuum orbitals are allowed to take on complex values.

The reasons for the choice of Gaussians located at real position $\vec{A}$, but with complex exponents $\alpha\theta^{-2}$ scaled in this particular fashion is explained in detail in Refs. 21, 22, and 17. Other choices are possible, but choosing all the basis function to have the form shown in Eq. (5), or the direct application of complex scaling to all of the electronic coordinates, has been shown to result in numerical instabilities in many-electron systems.[10]

The complex integrals and SCF codes used in the calculations presented here were based on symmetry adapted integrals and SCF codes developed by R. M. Pitzer[23] and kindly provided by him. The two-electron integrals and multicenter nuclear attraction integrals involving complex Gaussians can be reduced to expressions containing error functions of complex argument which we compute using Gautschi's algorithm.[24]

The basis set we used in these calculations is an extension of the $(8s,\ 2p)$ Gaussian basis given by Lie and Clementi.[25] The three s functions with largest exponents were contracted using the coefficients given by Lie and Clementi, and an additional s function with exponent equal to 0.029 12 was added. The contracted basis centered on the nuclei is thus $(7s,\ 2p)$, and these functions were used in both σ_g and σ_u symmetries. This real basis was augmented with a set of 15 complex P_z Gaussians with exponents whose moduli [α in Eq. (5)] are given by

$$5\Big/\left[2+\left[\frac{n-1}{40}\right]\right]^n\ ,\quad n=0,\ldots,14\ .$$

These functions were centered at the middle of the molecule and used only in σ_u symmetry. To avoid linear dependence problems at internuclear distances less than $1.7a_0$, the three complex P_z functions with largest exponents were removed and the two most diffuse s functions were included only in the σ_g orbital. It should be noted that the three P_z functions with largest exponents contributed relatively little in the calculations in which they were included.

The complex-scaling factor θ in Eq. (5) plays a role in these calculations quite analogous to the complex-scaling factor in a complex coordinates calculation, and we therefore treat it as a nonlinear variational parameter.[13,18] To make this nonlinear variational calculation a more efficient process we make use of a numerical analytic continuation of $E_{\text{CSCF}}(\theta)$, the CSCF energy as a function of θ. We begin by solving the complex SCF equations at several (typically four or five) values of $\theta=e^{i\gamma}$ with γ real valued. From these values we construct a rational fraction[26] approximation to $E_{\text{CSCF}}(\theta)$

$$E_{\text{CSCF}}(\theta)\simeq P_n(\theta)/Q_m(\theta)\ , \qquad (6)$$

where $P_n(\theta)$ and $Q_m(\theta)$ are polynomials and the rational fraction reproduces the computed values of $E_{\text{CSCF}}(\theta)$ exactly. We then make use of this rational fraction to find the stationary point at which

$$(dE_{\text{CSCF}}(\theta)/d\theta)_{\theta_{\text{stat}}}=0\ . \qquad (7)$$

In practice we find that $dE_{\text{CSCF}}(\theta)/d\theta$ is very small over a range of θ in a calculation employing a large basis set, and that a value of θ for which Eq. (7) is satisfied to within 10^{-8} a.u. is easily found by applying a steepest-descent algorithm to the magnitude of the derivative. In this way we often find that θ_{stat} has a modulus slightly different from 1. Figure 1 shows a typical "θ trajectory" and resulting stationary point.

Finally we will comment on the techniques involved in converging a CSCF calculation to self-consistency. First of all, as noted in Sec. II the open-shell coupling coefficients must be chosen so that the continuum orbital does not experience a potential due to itself. To start a calculation when no first guess is available, we begin by using the SCF wave function of the target to construct the static-exchange potential for electron scattering in our basis of real and complex Gaussians with θ

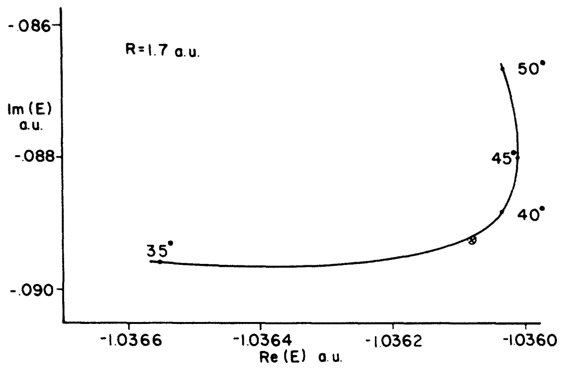


FIG. 1. E_{CSCF} for the $^2\Sigma_u^+$ state at $R=1.7a_0$ as a function of the scaling parameter $\theta=e^{i\gamma}$ for various values of γ. ⊗ denotes the stationary point from Eq. (7).

fixed. Diagonalizing the static-exchange Hamiltonian in that basis generally produces a solution for a continuum orbital which exhibits localization and clearly represents the resonance orbital. With that orbital as first guess for the resonance orbital and the neutral target orbitals as first guesses for the rest, we have found that simple iteration without extrapolations or level shifting converges readily. Once the CSCF solution is found at one value of θ, the orbitals from that solution can be used to form a good first guess for those at other θ values. In the calculations presented here we used both this technique and also found that we can follow the bound H_2^- wave function at large internuclear separations into the resonance region at smaller internuclear distances by using the results at one internuclear distance to start the CSCF calculation at another. Very near (within $0.05a_0$) the point where the width becomes nonzero convergence requires appreciably more iterations than in other ranges of internuclear separation.

IV. RESULTS OF CSCF CALCULATIONS ON THE $^2\Sigma_u^+$ SHAPE RESONANCE

We have performed CSCF calculations as described in Secs. II and III on the $^2\Sigma_u^+$ state of H_2^- at internuclear distances between 4.0 and $1.4a_0$. There have been several empirical determinations of the $^2\Sigma_u^+$ complex potential[12,27–29] and one *ab initio* calculation of the real part of the potential.[30] Nesbet[29] has noted that there is remarkable disagreement among these calculations, particularly for the real part of the potential.

Our results for the width function $\Gamma(R)$ are compared with the empirical determinations of Wadehra and Bardsley[12] and Chen and Peacher[27] in Fig. 2. Our results are in excellent agreement with the results Wadehra and Bardsley[12] obtained for the width by fitting the dissociative attachment cross section. Wadehra and Bardsley constrained their width function to vanish at $3.0a_0$, and the CSCF width goes to zero between 2.80 and 2.81 in our calculations. On the other hand the older Chen and Peacher[27] determination of the width from the isotope effect in dissociative attachment is in poor agreement with the Wadehra and Bardsley result and with ours. Also shown in Fig. 2 is the result of Moiseyev and Corcoran,[31] which was obtained by a CI calculation using complex coordinates with the coordinates of all three electrons scaled. Scaling all the electronic coordinates leads to numerical instability in general, and the variation of the energy as a function of the scaling parameters in the Moiseyev and Corcoran calculation is far more severe than that shown in Fig. 1. Considering the accuracy with which the CSCF method predicts the width of the $^2\Pi_g$ resonance[3] in N_2^-, it is surprising that the effects of correlation might affect the width as much as the Moiseyev and Corcoran calculation suggests. Clearly, further study will be necessary to resolve this

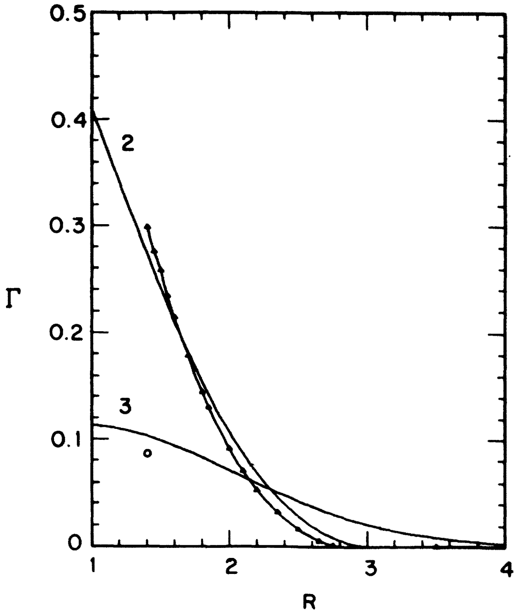


FIG. 2. Width as a function of internuclear distance from CSCF calculation (▲) and from Ref. 12 (curve 2) and Ref. 27 (curve 3). (○) is the theoretical result of Ref. 31.

discrepancy.

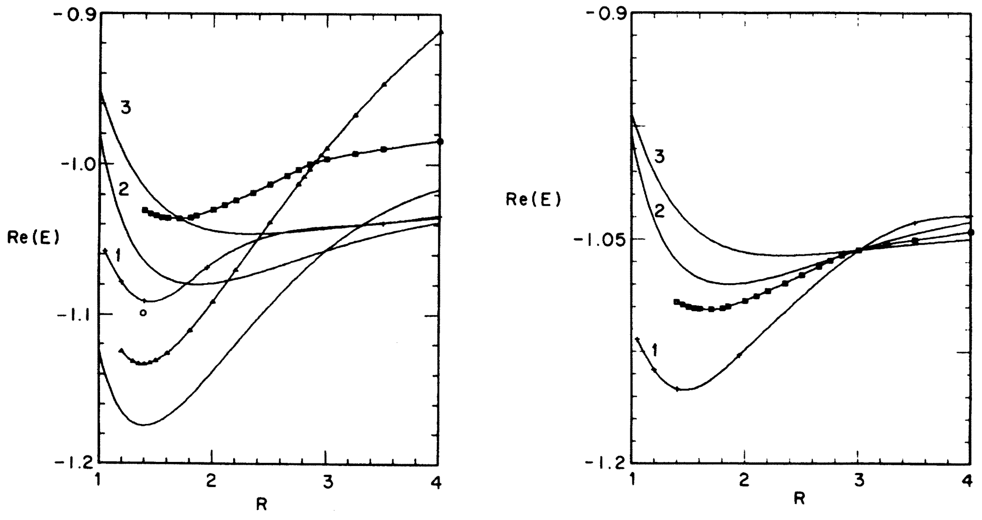
In Fig. 3(a) we compare the real part of the CSCF energy for H_2^- with other empirical and theoretical results, and also the SCF and exact values for the H_2 ground-state curve. The SCF and CSCF results are shifted upward by the neglect of correlation energy. The empirical results of Chen and Peacher[27] and those of Wadehra and Bardsley[12] show remarkable disagreement with one another and with the early stabilization calculations of Taylor and Harris[30] and Eliezer, Taylor, and Williams.[30] In Fig. 3(b) the H_2^- curves are shown shifted to coincide at $3.0a_0$. Although the CSCF curve agrees best in shape with that of Wadehra and Bardsley,[12] it is difficult to draw a definite conclusion on the basis of that comparison. The Eliezer, Taylor, and Williams[30] stabilization calculation included mainly target correlation but did allow the σ_g orbital to respond somewhat to the presence of the continuum electron. It is interesting to ask if the sharper minimum in their results arises predominantly from target correlation since the CSCF calculations, which also include response of the σ_g orbital but not target correlation, do not show such a sharp minimum. Again, more work is necessary to resolve these discrepancies.

Figures 4—7 demonstrate various aspects of the transition from the $^2\Sigma_u^+$ bound state of H_2^- at large distances to the resonance at smaller internuclear distance. In Fig. 4 we show an enlargement of the crossing region which reveals that the CSCF curve for H_2^- crosses the SCF curve for H_2 nearly $0.1a_0$ before the imaginary part of the CSCF energy becomes appreciably nonzero.

On the same graph we show an ordinary real-valued SCF calculation on H_2^- performed with the large basis of diffuse functions (with $\theta=1$) that are used in the CSCF calculations. Very near the point where the imaginary part of the energy in the CSCF calculation becomes nonzero, the σ_u orbital energy in the real-valued SCF calculation goes through zero. That orbital becomes very diffuse and an attempt to follow the SCF calculation in this large basis to smaller internuclear distances resulted in an H_2^- solution which is essentially the H_2 SCF wave function with a nearly zero energy σ_u orbital.

In the CSCF calculation the σ_u orbital energy need not ever have a value of exactly zero and moves out into the complex plane without reaching that point, as is shown in Fig. 5. The orbital remains quite well localized in the process. The σ_g orbital energy also becomes complex as the bound state becomes a resonance and that movement near the crossing point is shown in Fig. 6. Additional discussion of the SCF description of the "crossing region" together with several other examples of the bound state to resonance transition will be given in a future publication.

Figure 7 shows how the modulus of the σ_u orbital, plotted along the internuclear axis, changes



(a) (b)

FIG. 3. (a) SCF energy for H_2 ( ) and real part of CSCF energy for H_2^- (⊟). Curves 1, 2, and 3 for H_2^- are from Refs. 30, 12, and 27, respectively, and (○) is from Ref. 31. The lowest curve is the exact ground-state potential for H_2 of Kolos and Wolniewicz (Ref. 32); (b) H_2^- potentials shifted to coincide at $R=3.0a_0$.

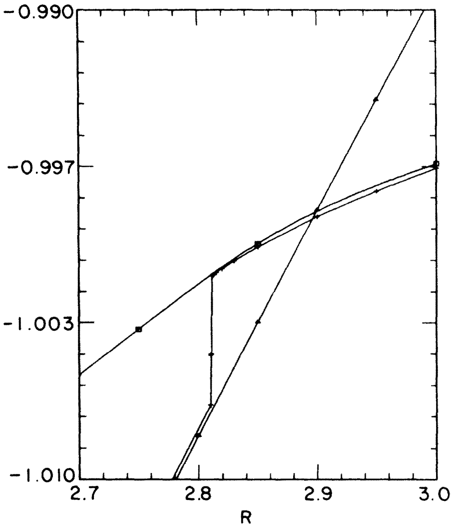


FIG. 4. SCF potentials in the crossing region: (⊟) CSCF for H_2^-, (▲) SCF for H_2, (+) real-valued SCF for H_2^- as described in text.

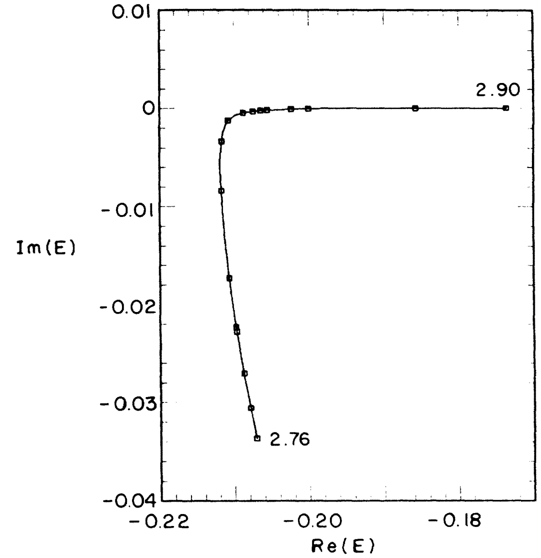


FIG. 6. Same as Fig. 5, but for σ_g orbital energy.

with internuclear separation R. At large R the orbital is well localized and has as its only prominent feature the cusps at the nuclear positions. At $R = 2.8a_0$ it begins to become more diffuse, and by $R = 1.7a_0$ has become exceedingly diffuse in accordance with the large width of the resonance (4.9 eV) at that point. All of the calculations which were done to form Fig. 7 were performed with the same value of the scaling parameter θ. Changing the scaling parameter can change the envelope of the wave function at larger values of the electronic coordinates but cannot change the qualitative trend shown in Fig. 7.

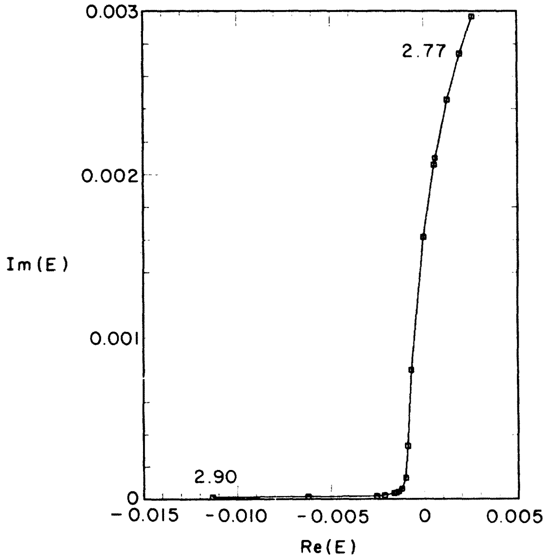


FIG. 5. Trace in the complex plane of the σ_u orbital energy from CSCF calculation as a function of internuclear distance near crossing point.

V. DISCUSSION

We have presented a description at the SCF level of the lowest $^2\Sigma_u^+$ resonance in electron-H_2 scattering. Our complex energy for this state is the location, in the Hartree-Fock approximation, of the corresponding resonance pole of the S matrix in the Born-Oppenheimer approximation. Comparison of our results with empirical determinations of the complex potential in terms of simple functional forms, and comparison with the two other *ab initio* theoretical results which are available, clearly shows that even for this relatively simple three-electron problem, the location of the resonance pole of the S matrix in the Born-Oppenheimer approximation as a function of internuclear separation is not accurately known.

It was pointed out in Sec. IV that even though our CSCF calculations using a large basis set almost undoubtedly give accurate values of the energy in the Hartree-Fock approximation, uncertainties in the other two *ab initio* theoretical calculations prevent us from drawing conclusions about the effects of correlation on the position and width of the resonance. However, the limited CI calcula-

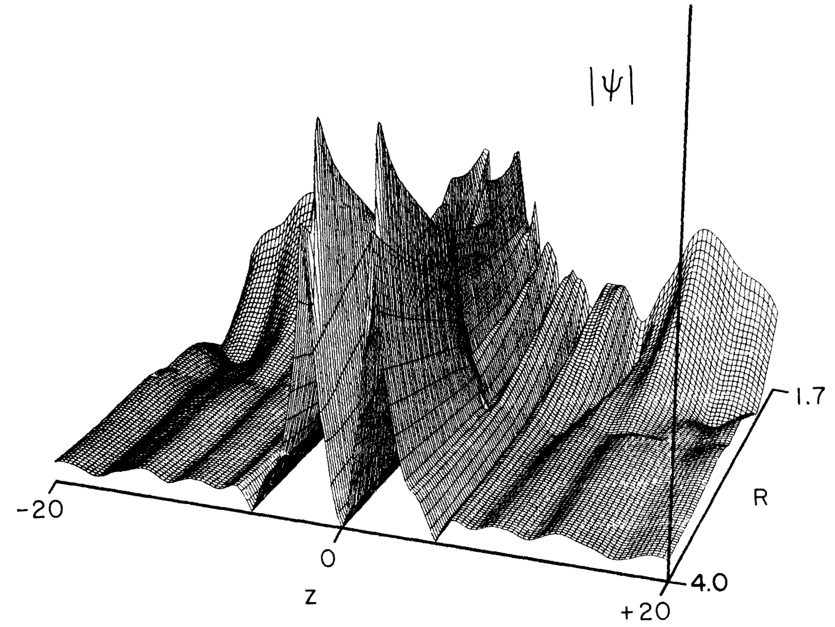


FIG. 7. Modulus of the σ_u orbital plotted along the internuclear axis z as a function of internuclear separation R.

tions of Taylor and co-workers[30] do suggest that the minimum in the real part of the complex potential for H_2^- may be made sharper by correlation.

Questions about the effect of correlation on the width are even more difficult to answer. The agreement of the CSCF width function with the recent empirical results of Wadehra and Bardsley[12] is consistent with the expectation based on CSCF results[3] on N_2^- that the CSCF approximation should be adequate for molecular shape resonances. Hazi, Rescigno, and Karila[5] used a width function which agrees with the CSCF calculation of Ref. 3 to compute cross sections for resonant vibrational excitation in e-N_2 scattering in reasonable agreement with experimental values. Therefore the fact that the complex CI calculation at one internuclear distance of Moiseyev and Corcoran[31] gave a far smaller width is puzzling because it suggests that the effects of correlation on the width may be drastic. However, the instability with respect to variation of the complex-scaling parameter shown in the Moiseyev and Corcoran calculation, and the small basis set employed [(5*s*, 3*p*, 1*d*) Gaussian basis contracted to (3*s*, 2*p*, 1*d*)], call their results into question. Speculation about the effect of correlation on the width of the resonance in this case appears to be unwarranted at present.

The CSCF wave functions we have obtained in these calculations form a logical starting point for more complete calculations on this system. Using the CSCF wave function at each internuclear distance as the reference configuration in a complex configuration interaction calculation, one can presumably perform calculations on this resonance with the same accuracy to be expected from a similar CI calculation on the ground state of a three-electron system. The CSCF wave function should provide the dominant contribution in a CI calculation except possibly near the crossing point where the CSCF energy first becomes complex as the nuclei are brought together. In this region the width is small, and may even be zero in the CSCF approximation but not at the CI level. We will report the results of CI calculations on the $H_2^-\ {}^2\Sigma_u^+$ shape resonance in a future publication.

Another question which deserves further attention is the question of the proper H_2 energy to subtract from the CSCF energy for H_2^- to give the position of the resonance. That question arises because N-electron SCF and $(N+1)$-electron CSCF calculations on the target and anion, respectively, will in general neglect different amounts of correlation energy. In order to circumvent this difficulty in an approximate way in SCF calculations using stabilization procedures to determine resonance position,[33] other workers have used as a reference energy the energy of a fictitious target molecule whose orbitals are those obtained in an SCF calculation on the anion and are therefore "relaxed" due

TABLE I. The real part of CSCF energy for $^2\Sigma_u^+$ resonance state of H_2^-, the width from the CSCF calculation, and SCF energies for H_2 using the same σ_g basis as in the CSCF calculations. All CSCF results are at θ_{stat} in Eq. (6), and atomic units are used throughout.

R	E_R	Γ	E_{SCF} (H_2)
1.40	−1.030 91	0.2987	
1.45	−1.032 96	0.2758	−1.132 74
1.50	−1.034 37	0.2581	−1.131 21
1.55	−1.035 32	0.2339	
1.60	−1.035 75	0.2142	−1.126 17
1.70	−1.036 08	0.1785	
1.80	−1.035 35	0.1444	−1.110 74
1.85	−1.034 20	0.1302	
2.00	−1.030 23	0.0913	−1.091 35
2.10	−1.027 11	0.0705	
2.20	−1.023 82	0.0530	−1.070 34
2.35	−1.018 76	0.0318	
2.50	−1.013 21	0.0161	−1.038 51
2.65	−1.007 50	0.0056	
2.75	−1.003 62	0.0012	−1.013 04
2.85	−0.999 94	0.0	−1.003 28
3.00	−0.996 55	0.0	−0.989 15
3.25	−0.992 66	0.0	−0.967 03
3.50	−0.989 67	0.0	−0.946 75
4.00	−0.984 11	0.0	−0.911 46

to the presence of the incident electron. It is not clear that this procedure is valid in CSCF calculations because all the orbitals have some complex component and the energy of the "polarized target" would consequently be complex. For this reason we present the SCF and CSCF energies in Table I without any modifications. Generalizations of the procedures used in Ref. 33 to give a reference energy are under investigation.

In spite of the problems and questions we have outlined, the CSCF method is a promising *ab initio* approach to the calculation of the complex energies of resonance states which are adequately approximated by a single-configuration wave function. The CSCF method is only slightly more difficult to implement than ordinary bound-state SCF calculations and should be applicable to the low-energy metastable anions of many small organic molecules.[34] In addition, CSCF calculations provide a logical starting point for complex CI calculations on resonances. Finally we note that accurate calculations of the complex potential for H_2^- are of particular interest in light of Nesbet's[29] recent suggestion that the complex potential model may not accurately describe the dynamics of nuclear motion in the case of such a broad shape resonance.

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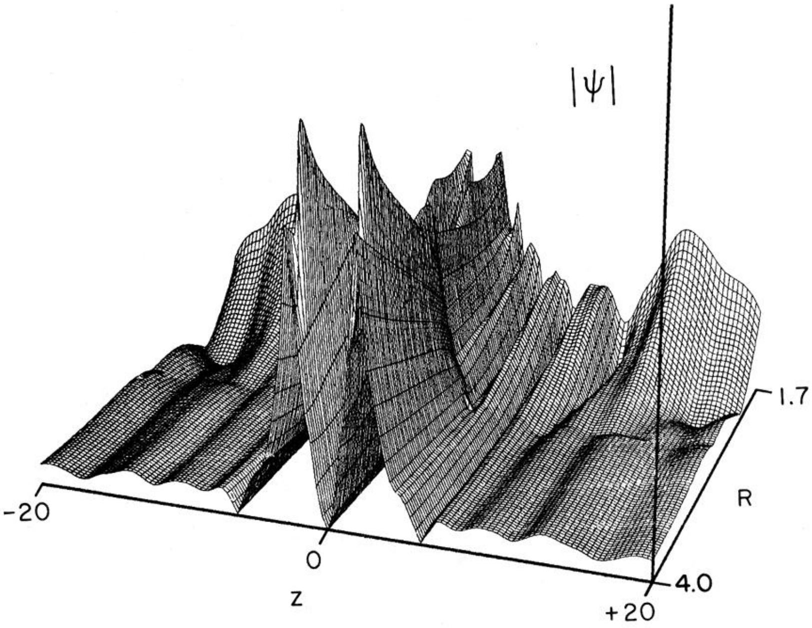

FIG. 7. Modulus of the σ_u orbital plotted along the internuclear axis z as a function of internuclear separation R.