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Projection-operator calculations for molecular shape resonances: The $^2\Sigma_u^+$ resonance in electron-hydrogen scattering

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A complete scattering-theoretic description of the $^2\Sigma_u^+$ shape resonance in fixed-nuclei electron-H_2 scattering is given within the framework of the projection-operator formalism of Feshbach. Polarization and correlation effects are included via the many-body optical-potential approach using the two-particle-hole Tamm-Dancoff approximation. The calculations result in a well-defined and physically meaningful separation of the T matrix and the eigenphase sum into a smooth background term and a resonant term, which varies rapidly with energy and internuclear distance. T matrices, eigenphase sums, and Feshbach resonance parameters ϵ_d, $\Gamma(E)$, and $\Delta(E)$ are obtained for a range of internuclear distances extending from the equilibrium distance of H_2 to 2.75 a.u. These fixed-nuclei data provide the basis for the *ab initio* calculation of cross sections for vibrational excitation and dissociative attachment in H_2 beyond the local-complex-potential approximation, to be reported in a forthcoming paper.

I. INTRODUCTION

The hydrogen molecule is the simplest closed-shell molecular target and has naturally received much attention in the development of the theory of electron-molecule scattering. The theoretical work up to 1980 has been comprehensively reviewed by Lane.[1] Apart from being a test case for fixed-nuclei electron-molecule scattering calculations,[1–5] the electron-H_2 collision system represents an interesting prototype for vibrational excitation and dissociative attachment. These inelastic and reactive collision processes are enhanced in H_2 in the 2–5 eV energy range by the existence of a shape resonance of $^2\Sigma_u^+$ symmetry.[6–8]

Early calculations[9] of the $^2\Sigma_u^+$ state of H_2^- were based on the Rayleigh-Ritz variational principle, disregarding the fact that this state is embedded in the continuum for $R \lesssim 3$ a.u. Bardsley *et al.*[10] chose a more rigorous approach by calculating the complex S-matrix pole corresponding to the $^2\Sigma_u^+$ shape resonance using Siegert state techniques. The complex resonance energy obtained in this way was adopted as the potential energy for the nuclear motion to calculate cross sections for vibrational excitation and dissociative attachment.[11] The stabilization method[12] was employed by Eliezer *et al.*[13] to calculate the potential-energy curve of the $^2\Sigma_u^+$ state of H_2^- as well as several other core-excited resonance states. Chen and Peacher[14] and Mizuno and Chen[15] determined the complex potential-energy curve of the $^2\Sigma_u^+$ state by fitting dissociative attachment and associative detachment data. A similar strategy was adopted by Bardsley and Wadehra,[16] who made an exhaustive study of rovibrational excitation and dissociative attachment in the local-complex-potential approximation. A detailed investigation of the associative detachment reaction in the local-complex-potential approximation has been performed by Bieniek and Dalgarno.[17] Recently, the energy and width of the $^2\Sigma_u^+$ resonance has also been calculated by self-consistent-field (SCF) and configuration-interaction (CI) techniques based on the complex-scaling method.[18,19] Up to date, the only true *ab initio* study of vibrational excitation of H_2 is the calculation of Klonover and Kaldor[20] based on the adiabatic-nuclei approximation using T-matrix elements obtained with an L^2-basis-set method.[21]

The $^2\Sigma_u^+$ resonance is very broad near the equilibrium geometry of H_2 and therefore difficult to characterize. This fact has recently been emphasized by Nesbet,[22] who points out that serious discrepancies exist between the $^2\Sigma_u^+$ potential-energy curves of the various studies mentioned above. These discrepancies are not only a consequence of the approximations involved in the computations, but are more fundamentally related to the fact that alternative definitions of the resonance energy and width may yield drastically differing results in the case of broad resonances.[23] When this happens, the local complex potential is necessarily no longer uniquely defined and fitting procedures based on the local-complex-potential approximation become meaningless.[22,23]

One might be tempted to abandon the resonance picture altogether and adopt a nonresonant formalism such as the standard rotational-vibrational close-coupling method.[1,24] This would not be wise, however, since for somewhat larger internuclear distances, near the crossing point of the H_2 and H_2^- potential-energy curves, the $^2\Sigma_u^+$ resonance becomes very narrow and has a decisive influence on the coupling of the electronic and nuclear motions. What is needed to resolve the problem is a description of resonances which is essentially complete and does not lose its meaning and uniqueness for very broad resonances.

Such a complete description of shape resonances has been developed recently[25,26] based on the projection-operator formalism of Feshbach.[27] The projection procedure requires the construction of a suitable discrete electronic state which approximates the resonance, using, for example, the stabilization method.[12,28] The formalism defines an exact decomposition of the T matrix and the eigenphase sum into a resonant and a background contribution, such that the background term becomes a smooth function of the energy and the internuclear distance, while rapid variations of the T matrix or the eigenphase sum are contained in the resonant term. The resonance is characterized by the discrete-state energy $\epsilon_d(R)$, the level-shift function $\Delta(E,R)$, and the width function $\Gamma(E,R)$. The method extends the Stieltjes-moment theory of Hazi[29–31] in that the background scattering T matrix as well as the angular distribution of the resonant scattering are explicitly obtained.

In the present work we show that this method provides an appropriate *ab initio* description of the ${}^2\Sigma_u^+$ shape resonance of $H_2{}^-$ over the whole range of internuclear distances from equilibrium to the crossing point, where the resonance becomes a bound state. In particular, we provide the data required for the treatment of the nuclear dynamics in electron-H_2 scattering beyond the local-complex-potential approximation. A detailed study of vibrational excitation and dissociative attachment cross sections, including isotope effects and dependence on the target vibrational state, will be given in a later paper.

II. FESHBACH PROJECTION-OPERATOR FORMALISM FOR SHAPE RESONANCES

As is well known, resonances in electron-atom and electron-molecule scattering can be divided into shape (or single-particle) and Feshbach (or core-excited) resonances.[32] The former are associated with the existence of a barrier of the electron-target interaction potential. The latter originate from closed-channel states embedded in open-channel continua.[27] While it is rather straightforward to isolate the core-excited resonances, which are usually narrow, it is not as obvious how to achieve a separation of the scattering amplitude or phase shift into a rapidly varying resonant part and a smoothly varying background part for shape resonances. A detailed discussion of this point for the simple case of potential scattering has been given recently.[25,33]

In electron-atom and electron-molecule scattering we face the additional problem that the target is a many-body system. Polarization of the target has an important effect on the position and width of shape resonances. It is possible, however, to reduce the electronic many-body scattering problem to an effective one-body scattering problem using the many-body optical potential formalism. As first shown by Bell and Squires,[34] the resulting energy-dependent, nonlocal, and, in general, complex optical potential is given by the irreducible self-energy part $\Sigma(E)$ of the many-body Green's-function formalism.[35] In what follows we apply projection-operator techniques[25,27] to this effective one-body problem to extract rapid variations of the phase shift due to shape resonances. Since a detailed description of the formalism including an illustrative application has been published recently,[26] only a brief outline is given here.

Assume that the effective potential Σ is such that the scattering amplitude exhibits an isolated single-particle resonance. Assume that a normalized square-integrable single-particle wave function $\phi_d(\vec{r})$ is given, which approximately describes the resonance. In practice, $\phi_d(\vec{r})$ may be constructed by the stabilization method.[28] We may then define projectors in the single-particle Hilbert space according to

$$Q=|\phi_d\rangle\langle\phi_d|\;,\quad P=1-Q\;. \tag{1}$$

The extension of the formalism to several discrete states is straightforward.[25] The P space is spanned by single-particle continuum states $|\hat{\vec{k}}^{(\pm)}\rangle$ constrained to be orthogonal to $|\phi_d\rangle$:

$$\langle\phi_d|\hat{\vec{k}}^{(\pm)}\rangle=0\;. \tag{2}$$

Here and in the following, the caret indicates orthogonality to the discrete state $|\phi_d\rangle$. The $|\hat{\vec{k}}^{(\pm)}\rangle$ can be constructed in closed form by orthogonalizing the free continuum to $|\phi_d\rangle$.[36,37]

Applying now the well-known Feshbach projection-operator techniques,[27] one obtains for the T matrix the desired separation into a resonant and a background term[25,33]

$$T(\vec{k}',\vec{k})=T_{\rm bg}(\vec{k}',\vec{k})+T_{\rm res}^{(F)}(\vec{k}',\vec{k})\;, \tag{3}$$

where (the superscript F stands for Feshbach)

$$T_{\rm bg}(\vec{k}',\vec{k})=\langle\vec{k}'|(PKP-K)|\hat{\vec{k}}^{(+)}\rangle+\langle\hat{\vec{k}}'^{(-)}|\Sigma|\hat{\phi}_{\vec{k}}^{(+)}\rangle\;, \tag{4}$$

$$T_{\rm res}^{(F)}(\vec{k}',\vec{k})=\langle\hat{\phi}_{\vec{k}'}^{(-)}|H|\phi_d\rangle[\tfrac{1}{2}k^2-\epsilon_d-F(k)]^{-1}\langle\phi_d|H|\hat{\phi}_{\vec{k}}^{(+)}\rangle\;, \tag{5}$$

with the abbreviations

$$H=K+\Sigma=-\tfrac{1}{2}\nabla^2+\Sigma\;, \tag{6}$$

$$\epsilon_d=\langle\phi_d|H|\phi_d\rangle\;, \tag{7}$$

$$F(k)=\langle\phi_d|H\hat{G}_{\rm bg}^{(+)}H|\phi_d\rangle\;. \tag{8}$$

The $|\hat{\phi}_{\vec{k}}^{(+)}\rangle$ are the background scattering states defined as the solutions of the projected Lippmann-Schwinger equation

$$|\hat{\phi}_{\vec{k}}^{(+)}\rangle=|\hat{\vec{k}}^{(+)}\rangle+\hat{G}_0^{(+)}\Sigma|\hat{\phi}_{\vec{k}}^{(+)}\rangle\;, \tag{9}$$

with

$$\hat{G}_0^{(+)}=P(\tfrac{1}{2}k^2-PKP+i\eta)^{-1}P\;. \tag{10}$$

The resolvent operator $\hat{G}_{\rm bg}^{(+)}$ in Eq. (8) is defined as

$$\hat{G}_{\rm bg}^{(+)}=P(\tfrac{1}{2}k^2-PHP+i\eta)^{-1}P\;. \tag{11}$$

A central quantity in the projection-operator formalism is the complex level-shift function $F(k)$ defined in Eq. (8). It defines the width function $\Gamma(E)$ and the real level-shift function $\Delta(E)$ via

$$\Delta(E)=\mathrm{Re}F(k)\ , \tag{12}$$

$$\Gamma(E)=-2\,\mathrm{Im}F(k) \tag{13}$$

for real positive $k=\sqrt{2E}$. The level shift for $E<0$ is given by $F(k)$ with positive imaginary k.

An important aspect of this formalism is that the orthogonality scattering[36,37] resulting from the constraint (2) and formally described by the nonlocal potential $PKP-K$ is treated exactly. Approximations have to be introduced, of course, when calculating the effective potential Σ and when solving the scattering problem. The above formalism guarantees, however, that for any given approximate Σ the orthogonality constraint (2) is fulfilled exactly and that T_{bg} and $T_{\mathrm{res}}^{(F)}$ of Eqs. (4) and (5) add exactly to the full T matrix obtained by solving the scattering problem without projection.

In practice, the calculations are performed in the partial-wave representation defined via

$$T(\vec{\mathrm{k}}\,',\vec{\mathrm{k}})=k^{-1}\sum_{l,l',m}T(k;l,l',m)Y_{l'm}(\Omega_{k'})Y_{lm}^{*}(\Omega_{k})\ , \tag{14}$$

where we have assumed a linear target molecule for simplicity. The resonant T matrix then reads

$$T_{\mathrm{res}}^{(F)}(k;l,l',m)=V_{kl'm}^{(-)}[\tfrac{1}{2}k^{2}-\epsilon_{d}-F(k)]^{-1}(V_{klm}^{(+)})^{*}\ , \tag{15}$$

with

$$V_{klm}^{(\pm)}=\langle\hat{\phi}_{klm}^{(\pm)}\,|\,H\,|\,\phi_{d}\rangle\ . \tag{16}$$

As shown in Ref. 26, the decomposition (3) of the T matrix is equivalent to a decomposition of the eigenphase sum

$$\delta^{\mathrm{sum}}=(2i)^{-1}\ln\det\underline{S}\ , \tag{17}$$

where $\underline{S}$ is the scattering matrix, into a resonant and a background term

$$\delta^{\mathrm{sum}}=\delta_{\mathrm{bg}}^{\mathrm{sum}}+\delta_{\mathrm{res}}^{\mathrm{sum}}\ . \tag{18}$$

The resonant eigenphase sum is given by the Breit-Wigner resonance formula with energy-dependent width and level shift[26,33,38]

$$\delta_{\mathrm{res}}^{\mathrm{sum}}=-\tan^{-1}\frac{\Gamma(E)/2}{E-\epsilon_{d}-\Delta(E)} \tag{19a}$$

and the integral resonant cross section in the fixed-nuclei limit is simply given by

$$\sigma=\frac{4\pi}{k^{2}}\nu\sin^{2}\delta_{\mathrm{res}}^{\mathrm{sum}}\ , \tag{19b}$$

where ν counts the spatial degeneracy of the discrete state. Equation (19b) follows from the fact that only a single resonant eigenphase is different from zero.

The essence of the method is to solve the projected Lippmann-Schwinger equation (9) instead of the original Lippmann-Schwinger equation. Since the orthogonal continuum states $|\,\hat{\vec{\mathrm{k}}}^{(\pm)}\rangle$ and the associated propagator $\hat{G}_{0}^{(\pm)}$ are given in closed form,[25,36,37] this is only slightly more complicated than the solution of the original scattering problem. In the present work the Schwinger variational principle[39–41] is used to solve the background scattering problem (see below). Once the background scattering states $|\,\hat{\phi}_{\vec{\mathrm{k}}}^{(\pm)}\rangle$ and the corresponding propagator $\hat{G}_{\mathrm{bg}}^{(\pm)}$ are given, the background scattering T matrix, the complex level shift, and the resonant T matrix are easily calculated. The formalism yields an exact separation of the T matrix into a resonant and a background term, which depends only on the choice of the discrete state $|\,\phi_{d}\rangle$. For an appropriately chosen discrete state, the background scattering T matrix is weakly dependent on energy and internuclear distance and the nuclear dynamics can thus be treated in the adiabatic-nuclei approximation.[1] The resonant scattering can be calculated beyond the Born-Oppenheimer approximation by taking account of the nonlocality of the effective potential governing the nuclear motion in the resonance state.[42–48] The possibility of including non-Born-Oppenheimer effects in resonant electron-molecule scattering in a unified and consistent manner is the major advantage of the projection-operator formalism.

III. COMPUTATIONAL ASPECTS

A. Approximation scheme for the optical potential

The energy-dependent optical potential[34,35] can be written as

$$\Sigma(E)=V_{\mathrm{SE}}+M(E)\ , \tag{20}$$

$$M(E)=[M(\infty)-V_{\mathrm{SE}}]+M^{\mathrm{I}}(E)+M^{\mathrm{II}}(E)\ . \tag{21}$$

The first term in Eq. (20) is the well-known static-exchange (SE) potential

$$V_{\mathrm{SE}}=V_{en}+\sum_{i}(J_{i}-K_{i})\ , \tag{22}$$

where V_{en} denotes the interaction potential of the projectile with the nuclei, and J_i and K_i are the usual Coulomb and exchange operators. $M(\infty)$ is the constant (energy-independent) term of the irreducible self-energy. The energy-dependent parts of the irreducible self-energy have the spectral representation[35]

$$M_{pq}^{\mathrm{I,II}}(E)=\sum\!\!\!\!\!\!\int_{n}\frac{m_{p}^{(n)}(m_{q}^{(n)})^{*}}{E-E^{(n)}\pm i\eta}\ , \tag{23}$$

where the indices p,q refer to a complete single-particle basis and the summation over n includes integration over the continuous part of the spectrum.

In many-body perturbation theory, Σ is defined via a diagrammatic perturbation expansion.[35] When the Hartree-Fock (HF) Hamiltonian is chosen as the unperturbed Hamiltonian, the perturbation expansion of $M^{\mathrm{I,II}}$ starts in second order. The perturbation expansion of the constant term $M(\infty)-V_{\mathrm{SE}}$ starts in third order in the residual electron-electron interaction.[49] The second-order optical potential has been employed by Klonover and Kaldor[20] in their comprehensive study of low-energy electron-H_2 scattering. More recently, it has been shown by Berman *et al.*[50] for the example of the $^2\Pi_g$ shape resonance in electron-N_2 scattering that the two-particle-hole

Tamm-Dancoff approximation (2ph-TDA) (Refs. 49 and 51) leads to a significantly improved description of the resonance position and width. The 2ph-TDA scheme represents an infinite partial summation of diagrams exact up to second order and can be derived in various ways.[49,51–54] It has been extensively used in the calculation of ionization potentials.[55] This approximation is also employed in the present study of e-H_2 scattering.

In the 2ph-TDA the poles $E^{(n)}$ of $M^{\mathrm{I}}(E)$ and $M^{\mathrm{II}}(E)$ in Eq. (23) are obtained separately by diagonalizing the Hamiltonian in the two-particle—one-hole (2p1h) and two-hole—one-particle (2h1p) configuration spaces. The amplitudes $m_p^{(n)}$ are obtained by multiplying the corresponding eigenvector elements with appropriate Coulomb matrix elements.[51] It can be shown[49,51] that the term $M^{\mathrm{I}}(E)$ accounts for the relaxation of the target electrons and the associated change in the pair-correlation energies in the target state. The term $M^{\mathrm{II}}(E)$ accounts for the increase of the pair-correlation energies due to the (temporary) attachment of an additional electron. Neglecting $M^{\mathrm{II}}(E)$ is equivalent to neglecting target-state correlation and performing a CI calculation on the negative ion including all 2p1h configurations. The inclusion of both $M^{\mathrm{I}}(E)$ and $M^{\mathrm{II}}(E)$ guarantees a balanced treatment of target correlation and polarization.[50,52]

In principle, the 2ph-TDA optical potential, like the second-order optical potential, has the correct analytic structure as defined in Eq. (23), i.e., it has simple poles infinitesimally above or below the real axis and cuts extending from the excitation and double-ionization thresholds to $\pm\infty$. The exact optical potential becomes complex for scattering energies above the first excitation threshold, thus accounting for the flux which is lost into inelastic channels. In practice, however, a discrete single-particle basis is used in the construction of $M^{\mathrm{I,II}}(E)$ and the cuts are replaced by sets of discrete poles on the real axis. In the present context this deficiency becomes relevant when we consider scattering energies above the lowest excitation threshold of the target molecule. Since the excitation energy of H_2 decreases rapidly with increasing internuclear distance, we are already faced with this problem of unphysical poles of $M(E)$ for rather low scattering energies. For $R=2.75$ a.u., for example, which is the largest internuclear distance considered in the present work, the lowest pole of $M^{\mathrm{I}}(E)$ is found at 2.55 eV.

To eliminate the unphysical poles of $M(E)$ in the energy region of interest, we resort to the usual recipe of averaging the rapidly fluctuating self-energy over a suitable inverval[56–58]

$$\langle M_{pq}(E)\rangle=\int_{-\infty}^{\infty}dE'\,\rho(E-E')M_{pq}(E')\ . \tag{24}$$

The simplest choice for the averaging function $\rho(E)$ is a Lorentzian

$$\rho(E)=\frac{1}{\pi}\frac{I}{E^2+I^2} \tag{25}$$

giving

$$\langle M_{pq}(E)\rangle=M_{pq}(E+iI)\ . \tag{26}$$

To avoid having a non-Hermitian self-energy operator for scattering energies below the excitation threshold, we adopt

$$\overline{M}_{pq}(E)=\mathrm{Re}[M_{pq}(E+iI)] \tag{27}$$

as our averaged self-energy. The averaging interval I is chosen to be just large enough to smooth out the unphysical poles of $M(E)$. When large basis sets are used in the construction of the 2ph-TDA self-energy, the unphysical poles are rather dense and a moderate averaging interval (typically 1 eV) is sufficient to make $\overline{M}(E)$ a smooth function of energy in the energy region of interest. For scattering energies E which are far from the poles of the self-energy part, the averaged self-energy $\overline{M}_{pq}(E)$ differs very little from $M_{pq}(E)$.

B. Solution of the scattering problem

We use the Schwinger variational principle[39] to solve the background scattering problem (9) and to construct the corresponding resolvent operator (11). This is equivalent to representing the optical potential in the separable form[40,41]

$$\Sigma^{(s)}=\sum_{i,j=1}^{N}\Sigma\,|\chi_i\rangle(\underline{\sigma}^{-1})_{ij}\langle\chi_j|\,\Sigma\ , \tag{28}$$

with

$$\sigma_{ij}=\langle\chi_i|\Sigma|\chi_j\rangle\ . \tag{29}$$

The functions $\langle\vec{r}\,|\chi_i\rangle$ are square-integrable energy-independent basis functions. With Σ replaced by $\Sigma^{(s)}$, the background scattering T matrix of Eq. (4) becomes[40,41]

$$T_{\mathrm{bg}}^{(s)}(\vec{k}\,',\vec{k})=\langle\vec{k}\,'|(PKP-K)|\hat{\vec{k}}^{(+)}\rangle+\sum_{i,j=1}^{N}\langle\hat{\vec{k}}'^{(-)}|\Sigma|\chi_i\rangle(\underline{N}^{-1})_{ij}\langle\chi_j|\Sigma|\hat{\vec{k}}^{(+)}\rangle, \tag{30}$$

with

$$N_{ij}=\langle\chi_i|(\Sigma-\Sigma\hat{G}_0^{(+)}\Sigma)|\chi_j\rangle\ . \tag{31}$$

The orthogonalized plane-wave states $|\hat{\vec{k}}^{(\pm)}\rangle$ and the Green's function $\hat{G}_0^{(+)}$ can be eliminated from Eqs. (30) and (31) using the closed-form expressions for these quantities, leaving us with standard matrix elements of Σ and $\Sigma G_0^{(+)}\Sigma$ with plane-wave states $|\vec{k}\rangle$ and basis states $|\chi_i\rangle$.[26] The background scattering states $|\hat{\phi}_{\vec{k}}^{(+)}\rangle$ and the Green's function $\hat{G}_{\mathrm{bg}}^{(+)}$ are obtained from the operator $T_{\mathrm{bg}}^{(s)}$ according to

$$|\hat{\phi}_{\vec{k}}^{(+)}\rangle=|\vec{k}\rangle+G_0^{(+)}T_{\mathrm{bg}}^{(s)}|\vec{k}\rangle\ , \tag{32}$$

$$\hat{G}_{\mathrm{bg}}^{(+)}=G_0^{(+)}+G_0^{(+)}T_{\mathrm{bg}}^{(s)}G_0^{(+)}\ . \tag{33}$$

The complex level shift is then directly obtained from Eqs. (5) and (8). For more details, the reader is referred to Ref. 26.

The main technical difficulty in the implementation of the Schwinger principle for electron-molecule scattering is the calculation of the matrix elements $\langle\chi_i|\Sigma|\vec{k}\rangle$ and

$\langle \chi_i | \Sigma G_0^{(+)} \Sigma | \chi_j \rangle$. Here we simplify the problem by inserting a large "quadrature basis" between the operators Σ and $G_0^{(+)}$, with the result that only matrix elements of Σ and $G_0^{(+)}$ are needed. The convergence of such insertions has been studied by Watson *et al.*[3] In the same way the "bound-continuum" matrix elements $\langle \chi_i | \Sigma | \vec{k} \rangle$ are reduced to "bound-bound" matrix elements of Σ and "bound-continuum" overlaps $\langle \chi_i | \vec{k} \rangle$. The matrix elements of Σ are obtained using standard bound-state codes for Gaussian basis functions. The bound-continuum overlaps and the matrix elements of the free Green's function

$$\langle \chi_i | G_0^{(+)}(k) | \chi_j \rangle = 2 \int d^3q \frac{\langle \chi_i | \vec{q} \rangle \langle \vec{q} | \chi_j \rangle}{k^2 - q^2 + i\eta} \tag{34}$$

can be calculated analytically for Gaussian basis functions.[59,60]

In the special case that the quadrature basis is identical to the "scattering basis" $\{ \langle \vec{r} | \chi_i \rangle \}$ introduced in Eq. (28), the T matrix of the present method reduces to the separable T matrix introduced by Rescigno *et al.*[21] This corresponds to replacing $\Sigma^{(s)}$ of Eq. (28) by the "truncated" potential

$$\Sigma^{(t)} = \sum_{i,j=1}^{N} | \chi_i \rangle \sigma_{ij} \langle \chi_j | \ . \tag{35}$$

The comparison of the results obtained with the approximate potentials (28) and (35) provides a certain check of the errors introduced by approximating the scattering potential in a basis.

For the calculation of fixed-nuclei eigenphases and cross sections only positive scattering energies E are of interest. For the treatment of nuclear dynamics in the projection-operator approach, on the other hand, we need in general also the real level-shift function $\Delta(E)$ for negative energies, since bound electronic states are given by the negative-energy solutions of

$$E - \epsilon_d - \Delta(E) = 0 \ . \tag{36}$$

The bound-state potential-energy curves are needed for the treatment of the dynamics of processes such as dissociative attachment and associative detachment.

The branch of $\Delta(E)$ which yields bound states according to Eq. (36) is obtained by analytically continuing $F(k)$ of Eq. (8) onto the positive imaginary k axis.[61] Within the approximation scheme described above, the k dependence of $F(k)$ is completely determined by the matrix elements (34) of the free Green's function. The analytic formulas which express the matrix elements (34) in terms of the complex error function[59,60] define the analytic continuation of these matrix elements into the complex momentum plane. In fact, all matrix elements are entire analytic functions of k. The existing codes[60] for the computation of the matrix elements of $G_0^{(+)}$ need to be modified only marginally to obtain the analytically continued matrix elements. More details are given elsewhere.[62]

C. Computational details

Calculations have been performed for seven internuclear distances of the H_2 molecule, namely $R = 1.4014$, 1.6, 1.8, 2.0, 2.2., 2.5, and 2.75 a.u. For each internuclear distance a HF calculation has been performed which defines the static-exchange potential and the single-particle manifold used in constructing the optical potential. The atomic basis set is the uncontracted $10s,5p,1d$ Gaussian basis of Schulman and Kaufman[63] and is given in Table I.

After transformation of the one- and two-electron integrals to the HF single-particle basis, the static-exchange potential and the 2ph-TDA self-energy are constructed as briefly indicated in Sec. III A. The complete space of 2p1h and 2h1p excitations is exhausted in the 2ph-TDA calculation. More details concerning the numerical implementation of the 2ph-TDA can be found in Ref. 55. An important aspect is that the poles and residues of the energy-dependent self-energy [see Eq. (23)] need to be evaluated only once for each internuclear distance. From these data, the matrix elements of $M(E)$ are readily evaluated for each scattering energy E. To obtain the representation of $M(E)$ in the quadrature basis $\{ \langle \vec{r} | \alpha \rangle \}$, which is in general larger than the HF single-particle basis, matrix elements of the type $\langle \alpha i | r_{12}^{-1} | jl \rangle$ are need-

TABLE I. Gaussian basis sets for e-H_2 scattering. The exponents of the basis functions on the atoms are listed.

	Hartree-Fock set:
s	600, 192, 64.224, 9.9142, 2.5988, 1.0676, 0.4384, 0.1569, 0.05, 0.017
p_x, p_y, p_z	4, 2, 0.9, 0.4, 0.2
$d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, d_{yz}$	2
	Discrete-state set:
s	600, 192, 64.224, 9.9142, 2.5988, 1.0676, 0.4384
p_z	4, 2, 0.9, 0.4, 0.2
d_{zz}	2
	Scattering set:
	The s, p_z, d_{zz} functions of the Hartree-Fock set
	Quadrature set:
s	The s basis of the scattering set plus 0.006, 0.002
p_z	The p_z basis of the scattering set plus 0.07, 0.02
d_{zz}	The d_{zz} basis of the scattering set plus 0.7, 0.2

ed, where the indices i,j,l refer to HF orbitals and α is a Gaussian orbital of the quadrature basis.

Once the scattering potential is defined, we may proceed to select a suitable discrete state by the stabilization method.[12,28,32] In the present work the discrete state is defined for the static-exchange potential and is thus independent of the scattering energy E. In previous work on the $^2\Pi_g$ shape resonance of N_2 we have preferred to choose an energy-dependent discrete state,[26] obtained by a stabilization calculation for the energy-dependent 2ph-TDA optical potential. In e-H_2 scattering both definitions yield very similar results and we prefer the former definition for the sake of conceptual simplicity. We diagonalize the single-particle Hamiltonian $H=K+V_{SE}$ in discrete Gaussian basis sets of various sizes, looking for approximately stable eigenvalues of σ_u symmetry. It is found that after the removal of the three most diffuse s orbitals with exponents 0.017, 0.05, and 0.1569 the lowest σ_u orbital energy becomes approximately stable with respect to further restrictions of the basis. Removal of p-type functions had no significant effect on the σ_u orbital energy. The discrete-state basis set was thus taken to be the atomic basis set minus the three most diffuse s-type orbitals. While the selection of the discrete state may appear somewhat arbitrary to the reader at this stage, we stress that the justification is provided by the final results of the calculation. As will be seen below, the discrete state just selected leads indeed to a clean and physically sensible separation of the $^2\Sigma_u^+$ eigenphase sum into a resonant and a background term for all internuclear distances considered.

Moreover, we have the important criterion that the discrete state should be "quasidiabatic", i.e., the associated molecular orbital coefficients should be weakly dependent on the internuclear distance. Indeed, the R dependence of the wave function of the above discrete state consists mainly in the "floating" of the atomic orbitals with the nuclei. In contrast to the discrete state, the σ_u molecular orbitals calculated in the full basis including the diffuse atomic orbitals exhibit strongly varying molecular orbital coefficients when the internuclear distance changes.

The next computational step is the solution of the background scattering problem (9) using the Schwinger variational principle. The scattering basis was chosen to be identical with the HF atomic basis set described above. We have checked that the calculated eigenphase sum is insensitive to further extensions of the scattering basis. The quadrature basis set is obtained by augmenting the scattering basis with diffuse functions of s, p, and d types (see Table I). Again, we have checked that the calculated eigenphase sum is insensitive to further extensions of this basis. In fact, the results obtained with the Schwinger-type potential $\Sigma^{(s)}$ of Eq. (28) and the truncated potential $\Sigma^{(t)}$ of Eq. (35) are nearly identical, indicating that the errors introduced by approximating the scattering potential in a basis are minor.

The background scattering states $|\hat{\phi}_{\vec{k}}^{(+)}\rangle$ and the background Green's function $\hat{G}_{bg}^{(+)}$ are next constructed from Eqs. (32) and (33) using the representation of $T_{bg}^{(s)}$ in the quadrature basis. The width and level-shift functions are then obtained directly from Eqs. (8), (12), and (13) and the discrete-continuum coupling elements from Eq. (16). The resonant T matrix $T_{res}^{(F)}$ and the corresponding eigenphase sum are given by Eqs. (15) and (19a).

IV. RESULTS

Since resonant features in low-energy e-H_2 scattering are observed only in the $^2\Sigma_u^+$ eigenphase sum,[1-5] the calculations have been restricted to this symmetry. To assess the importance of polarization and correlation effects, scattering calculations have been performed for three potentials of increasing sophistication, namely the static-exchange, the second-order, and the 2ph-TDA optical potentials. The results obtained for the $^2\Sigma_u^+$ eigenphase sum at $R=1.4014$ a.u., the equilibrium geometry of H_2,[64] using the Schwinger variational principle are given in Fig. 1 and Table II. (Eigenphase sums are in units of radians throughout.) The solid line in Fig. 1 shows the static-exchange result in comparison with the benchmark static-exchange calculation of Collins, Robb, and Morrison[2] (stars). The present results are consistently somewhat too low, which we attribute to basis set limitations in our calculation, but are nevertheless in good overall agreement with the results of Ref. 2 and the R-matrix calculation of Noble, Burke, and Salvini[65] (see also Table II). This indicates the reliability of the L^2 representation of the potential used in our calculations. The short-dashed and long-dashed curves show the eigenphase sums obtained with the second-order and the 2ph-TDA optical potentials, respectively. Apart from differences in the basis sets, the former result should be identical with the result of Klonover and Kaldor.[20] It is seen that many-body effects increase the eigenphase sum considerably, the main part of the correction being obtained already in second order. As will become clear below, the increase of the eigenphase sum is mainly a consequence of the lowering of the resonance energy by polarization effects.

Ab initio calculations on e-H_2 scattering which include polarization effects via a Feshbach-type optical potential or a nonadiabatic polarization potential have been published recently.[4,5] In Fig. 2 we compare the $^2\Sigma_u^+$ cross section obtained with the 2ph-TDA optical potential with the results of Schneider and Collins[4] and Gibson and Morrison.[5] While there is good overall agreement between the

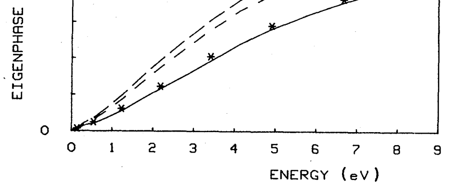

FIG. 1. The $^2\Sigma_u^+$ eigenphase sum for e-H_2 scattering. Solid line: static-exchange approximation; short-dashed curve: second-order optical potential; long-dashed curve: 2ph-TDA optical potential. Stars are the static-exchange results of Ref. 2.

TABLE II. Eigenphase sum for the $^2\Sigma_u^+$ symmetry in e-H_2 scattering at $R=1.4014$ a.u. obtained in the static-exchange (SE) approximation and with the second-order and 2ph-TDA optical potentials.

k (a.u.)	E (eV)	SE[a]	SE[b]	SE	Second order	2ph-TDA
0.1	0.136	0.0134	0.0128	0.0065	0.0098	0.0111
0.2	0.544	0.0493	0.0481	0.0417	0.0639	0.0724
0.3	1.224	0.1233	0.1204	0.1099	0.1711	0.1933
0.4	2.177	0.2459	0.2421	0.2329	0.3487	0.3880
0.5	3.401	0.4084	0.4032	0.3843	0.5561	0.6110
0.6	4.898	0.5797	0.5694	0.5620	0.7507	0.8099
0.7	6.666	0.7269	0.7239	0.7096	0.8900	0.9522
0.8	8.707	0.8361	0.8086	0.8291	0.9928	1.0681

[a] Reference 2.
[b] Reference 65.

latter two and the present calculations, the resonant rise of the cross section occurs at higher energy in our results. The difference between the present cross section and that of Ref. 4 is much larger than the difference found in the static-exchange approximation and thus reflects differences in the polarization-correlation potential. We attribute the differences to target correlation effects which are neglected in Refs. 4 and 5, but are included in the 2ph-TDA.[51,52] Target correlation has the tendency to increase the energy of shape resonances.[50]

Figure 3 shows the $^2\Sigma_u^+$ eigenphase sum calculated with the 2ph-TDA optical potential for seven internuclear distances ranging from $R=1.4014$ to 2.75 a.u. As was mentioned earlier, the optical potential has to be energy averaged for larger internuclear distances, since unphysical poles of $\Sigma(E)$ appear in the energy region considered. No averaging was necessary for $R=1.4014$, 1.6, and 1.8 a.u. For the larger distances the averaging interval I [see Eqs. (24)—(27)] was chosen just large enough to smooth out the pole structure of $\Sigma(E)$ in the energy range of interest. The appropriate averaging interval was found to be $I=2.0$ eV for $R=2.0$, 2.2, and 2.5 a.u. and $I=3.0$ eV for $R=2.75$ a.u.

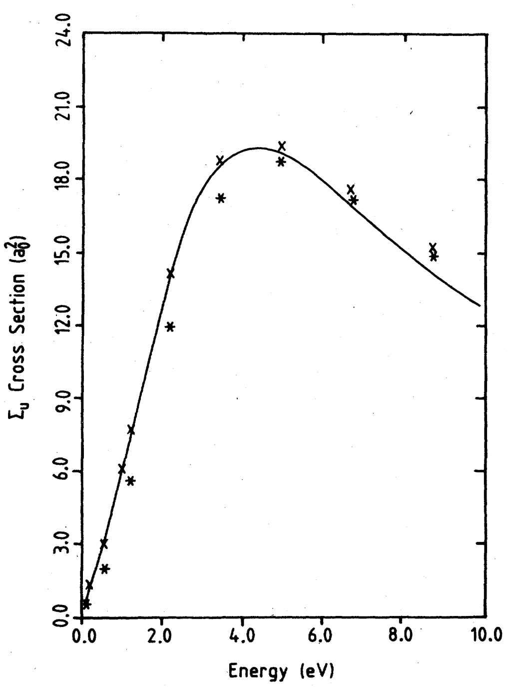

FIG. 2. The $^2\Sigma_u^+$ cross section obtained with the 2ph-TDA optical potential (stars) in comparison with the static-exchange-polarization results of Collins and Schneider (Ref. 4) (crosses) and Gibson and Morrison (Ref. 5) (solid line).

Figure 3 illustrates how the resonance in $^2\Sigma_u^+$ symmetry moves to lower energy and sharpens dramatically when the internuclear distance increases. While the resonance is hardly discernable as such at the equilibrium distance of H_2, one observes a very sharp low-energy Breit-Wigner resonance at $R=2.75$ a.u. For distances larger than about 2.9 a.u. the $^2\Sigma_u^+$ state becomes bound and the resonant increase of the phase shift disappears. The strong R dependence of the $^2\Sigma_u^+$ phase shift illustrated in Fig. 3 is the origin of the interesting dynamical effects in low-energy e-H_2 collisions, i.e., vibrational excitation and dissociative attachment.

Let us now turn to the main object of the present calculations, namely the application of the projection-operator formalism to the $^2\Sigma_u^+$ shape resonance. Figure 4 shows the decomposition of the eigenphase sum (solid line) into a resonant term (short dashes) and a background term (long dashes) for the three representative distances $R=1.4014$, 2.0, and 2.75 a.u. The decomposition is shown both on the static-exchange and the 2ph-TDA levels of approximation. In all cases the lower (upper) curve of a given

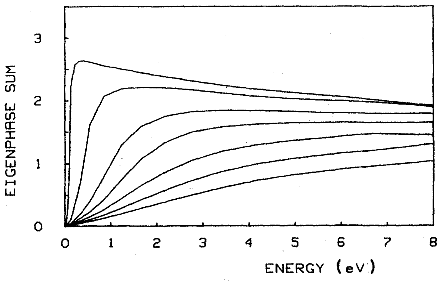

FIG. 3. The $^2\Sigma_u^+$ eigenphase sum for e-H_2 scattering obtained with the 2ph-TDA optical potential as a function of energy and internuclear distance. The curves correspond, from bottom to top, to the following internuclear distances (in a.u.): 1.4014, 1.6, 1.8, 2.0, 2.2., 2.5, and 2.75.

line type gives the static-exchange (2ph-TDA) result. The important observations we can make when considering Fig. 4 are the following: (i) The background eigenphase sum is a smooth function of energy, decreasing approximately linearly with energy; (ii) for a given energy, the background eigenphase sum is independent of the internuclear distance to a very good approximation [note the different scales in Figs. 4(a)–4(c)]; and (iii) the background eigenphase sum is virtually unaffected by polarization and correlation effects.

To illustrate the important point (ii) more clearly, we show in Fig. 5 the resonant and background eigenphase sums (calculated in the 2ph-TDA) separately for all internuclear distances. The sum of these gives the full $^2\Sigma_u^+$ eigenphase sum shown in Fig. 3. The background phase shift is seen to be nearly independent of R, while the resonant phase shift is strongly R dependent. By construction, $\delta_{\rm res}^{\rm sum}(E)$ rises by π rad from $E=0$ to ∞, while $\delta_{\rm bg}^{\rm sum}(E)$ decreases by π rad as E goes from zero to infinity. For internuclear distances near the equilibrium distance of H_2, the increase of $\delta_{\rm res}^{\rm sum}$ is canceled to a large extent by the decrease of $\delta_{\rm bg}^{\rm sum}$, resulting in a total eigenphase sum which exhibits hardly any resonant behavior. For large internuclear distances, on the other hand, $\delta_{\rm res}^{\rm sum}$ rises by π rad within such a narrow energy range that the variation of $\delta_{\rm bg}^{\rm sum}$ with energy is negligible. Therefore the full eigenphase sum clearly exhibits the existence of the resonance.

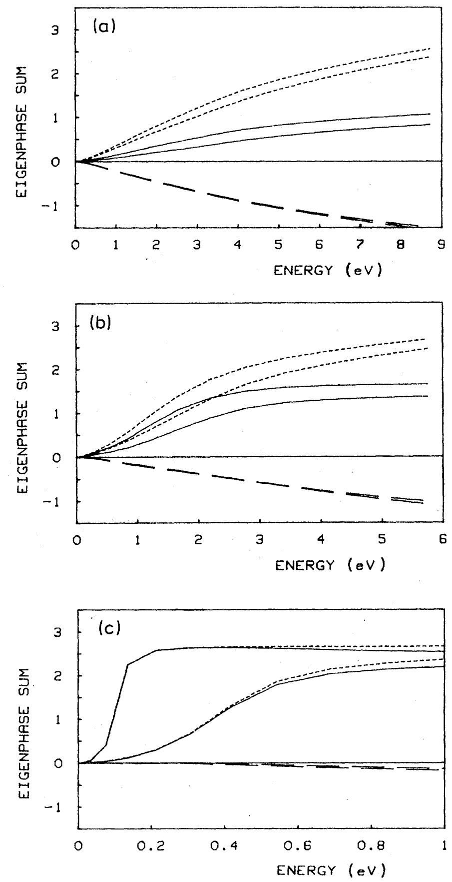

FIG. 4. Decomposition of the $^2\Sigma_u^+$ eigenphase sum into resonant and background contributions via the Feshbach projection-operator formalism for three representative internuclear distances, (a) $R=1.4014$ a.u., (b) $R=2.0$ a.u., and (c) $R=2.75$ a.u. Resonant phase shift is given by the short-dashed curve, background phase shift by the long-dashed curve. The sum of both is the full $^2\Sigma_u^+$ phase shift (solid line). In all three figures the upper curve of a given line type refers to the 2ph-TDA, the lower curve to the static-exchange approximation.

These results show that we have indeed succeeded in separating the eigenphase sum into a resonant and a background term in a physically meaningful manner for the whole range of internuclear distances considered. The strong R dependence of the $^2\Sigma_u^+$ eigenphase sum illustrated in Fig. 3 is fully contained in the resonant term. The sensitivity to polarization and correlation effects, which is typical for resonant eigenphase sums, is also restricted to the resonant term. The background term is thus the uninteresting part of the eigenphase sum as far as many-body effects and the effects of nuclear dynamics in e-molecule scattering are concerned. While the decomposition seems to be pointless at $R=1.4014$ a.u. [Fig. 4(a)], where $\delta_{\rm res}^{\rm sum}(E)$ exhibits hardly more structure than $\delta_{\rm bg}^{\rm sum}(E)$ and both are of about the same size, the meaning of the decomposition becomes obvious for $R=2.75$ a.u. [Fig. 4(c)], where $\delta_{\rm res}^{\rm sum}(E)$ describes a nearly ideal Breit-Wigner resonance, i.e., a sharp rise by π rad, while $\delta_{\rm bg}^{\rm sum}$ is very small and almost constant in the energy range of interest. A case qualitatively similar to Fig. 4(c) is the $^2\Pi_g$ resonance in e-N_2 scattering at the equilibrium geometry of N_2, which is also a comparatively narrow resonance.[26] The present results demonstrate, for the first time, the possibility of a well-defined decomposition of the eigenphase sum also for a very broad shape resonance.

As has been discussed in Sec. II, the resonant eigenphase sum is given by the simple Breit-Wigner formula (19a) with energy-dependent width and level-shift functions $\Gamma(E)$ and $\Delta(E)$. The discrete-state energy $\epsilon_d=\langle\phi_d\,|\,H\,|\,\phi_d\rangle$ is also a function of the scattering energy E owing to the energy dependence of the optical potential, resulting from the existence of closed excitation channels. Figure 6 shows ϵ_d, Γ, and Δ calculated with the 2ph-TDA potential as a function of energy for the seven internuclear distances considered here. It is seen that ϵ_d decreases monotonically with R. The energy dependence

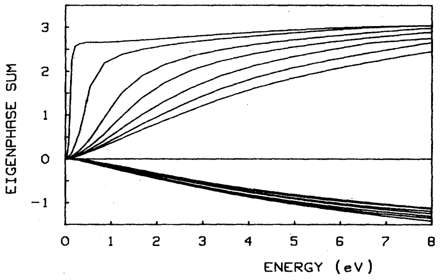

FIG. 5. Resonant (upper curves) and background (lower curves) eigenphase sums calculated in the 2ph-TDA as a function of energy and internuclear distance.

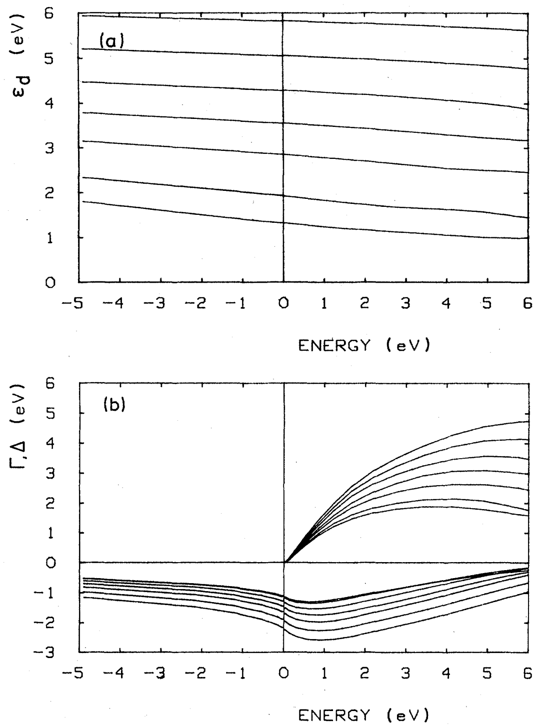

FIG. 6. Discrete-state energy ϵ_d (a) and width Γ [(b), upper curves] and level shift Δ [(b), lower curves] as a function of energy and internuclear distance. The curves correspond, from top to bottom (ϵ_d,Γ) or bottom to top ($\triangle$), to the internuclear distances given in the caption of Fig. 3.

of ϵ_d is rather weak (it is much more pronounced in N_2,[26] which is a more polarizable target). Figure 6(b) shows the corresponding width and level-shift functions as a function of E and R. Γ and the absolute value of Δ decrease monotonically with R, i.e., the uppermost (lowest) curve for $\Gamma(\Delta)$ corresponds to $R=1.4014$ a.u., the lowest (highest) curve to $R=2.75$ a.u. Note that both the width and the level shift are quite large and strongly energy dependent. In particular, $\Gamma(E)$ rises rather steeply for small E and $\Delta(E)$ exhibits a significant energy dependence near threshold. The width and level-shift functions obtained in the static-exchange approximation are very similar to those in Fig. 6(b) and are therefore not shown separately.

The level-shift function Δ for negative energies is obtained by direct analytic continuation as described in Sec. III B; the usual Hilbert-transform relationship[29–31,45,46] is not used. Strictly speaking, $\Delta(E)$ is *not* the Hilbert transform of $\Gamma(E)$, as is usually assumed. This is a consequence of polarization effects which cause the optical potential to be energy dependent (see discussion in Ref. 26). In the case of e-H_2 scattering, however, the deviation of Δ from the Hilbert transform of Γ is probably small due to the weakness of polarization effects. However, an important practical advantage of the direct calculation of $\Delta(E)$ from Eqs. (8) and (12) as opposed to the Hilbert transformation of $\Gamma(E)$ is the fact that $\Gamma(E)$ is not needed for all energies where it is nonzero. As can be seen in Fig. 6(b), $\Gamma(E)$ starts to decrease only at about 5 eV; it would thus be necessary to compute $\Gamma(E)$ up to quite high energies in order to obtain an accurate level shift by the Hilbert transformation of $\Gamma(E)$.

To complete the fixed-nuclei description of the ${}^2\Sigma_u^+$ resonance, we present information on the angular distribution of the resonant and background scattering in Table III. The angular distribution of the background scattering is characterized by the background K matrix, defined as

$$\underline{K}_{\rm bg}=-\pi\underline{T}_{\rm bg}(\underline{1}-i\pi\underline{T}_{\rm bg})^{-1}\ ,$$

with $\underline{T}_{\rm bg}$ given by Eq. (30) in the partial-wave representation (14). The angular distribution of the resonant scattering is completely determined by the discrete-continuum coupling elements $V_{klm}^{(+)}(E,R)$ defined in Eq. (16). Table III shows these data (calculated with the 2ph-TDA potential) for the equilibrium geometry of H_2 and three energies in the vicinity of the resonance position (defined by $\delta_{\rm res}^{\rm sum}=\pi/2$). The results confirm the well-known fact that the ${}^2\Sigma_u^+$ resonance is a nearly pure p-wave resonance. The background scattering is also strongly dominated by the $l=1$ partial wave. For completeness, we include in Table

TABLE III. Angular dependence of resonant and background scattering for the ${}^2\Sigma_u^+$ symmetry in e-H_2 scattering at $R=1.4014$ a.u. (Numbers in parentheses indicate powers of ten.)

	$k=0.3$ a.u. ($E=1.224$ eV)			$k=0.5$ a.u. ($E=3.401$ eV)			$k=0.65$ a.u. ($E=5.748$ eV)		
	−2.73(−1)			−9.32(−1)			−2.24		
$\underline{K}_{\rm bg}$	−8.00(−4)	−3.37(−3)		−4.56(−3)	−9.53(−3)		−2.69(−2)	1.25(−3)	
($l,l'=1,3,5$)	−4.97(−7)	−1.52(−6)	−3.67(−10)	−2.11(−5)	−1.03(−5)	1.43(−8)	−1.70(−4)	9.80(−5)	−7.42(−8)
	l	Re $V_{klm}^{(+)}$	Im $V_{klm}^{(+)}$	l	Re $V_{klm}^{(+)}$	Im $V_{klm}^{(+)}$	l	Re $V_{klm}^{(+)}$	Im $V_{klm}^{(+)}$
$V_{klm}^{(+)}$ (a.u.)	1	−1.04(−1)	2.84(−2)	1	−1.11(−1)	1.03(−1)	1	−6.78(−2)	1.52(−1)
($m=1$)	3	−6.30(−4)	8.33(−5)	3	−2.52(−3)	6.49(−4)	3	−1.82(−3)	1.69(−3)
	5	−7.74(−6)	5.15(−8)	5	−5.62(−6)	2.25(−6)	5	−1.13(−5)	1.26(−5)
$\delta_{\rm bg}^{\rm sum}$			−0.2695			−0.7597			−1.1081
ϵ_d (eV)			5.787			5.719			5.626
Γ (eV)			1.997			3.906			4.725
Δ (eV)			−2.561			−1.921			−1.056
$\delta_{\rm res}^{\rm sum}$			0.4627			1.3706			2.0333

III the eigenphase sums and the resonance parameters for these particular energies. Our calculations show that the angular distribution of the ${}^2\Sigma_u^+$ symmetry does not change appreciably with internuclear distance. The dominance of p-wave scattering exhibited in Table III is found for the whole range of internuclear distances considered here.

V. DISCUSSION AND CONCLUSIONS

We have obtained a separation of the fixed-nuclei T matrix and eigenphase sum for e-H_2 scattering into a smooth background term and a resonant term which varies rapidly with energy and internuclear distance. The relevance of this separation lies in the treatment of nuclear motion in e-molecule scattering. Owing to its weak dependence on E and R, the background scattering T matrix can be treated in the adiabatic-nuclei approximation.[1,66] The resonant T matrix, on the other hand, can be calculated to a higher level of sophistication by properly treating the nuclear dynamics in the short-lived negative ion state, which is governed by an energy-dependent, complex, and nonlocal potential.[42–48] The fixed-nuclei Feshbach resonance parameters $\epsilon_d(R)$, $\Gamma(E,R)$, and $\Delta(E,R)$ are sufficient to construct the nonlocal potential.[46] The Feshbach formalism allows us to treat vibrational excitation of H_2 beyond the usually employed adiabatic-nuclei approximation[20] and provides, in particular, the basis for the *ab initio* calculation of dissociative attachment in H_2.[67] The dynamics of H-H$^-$ collisions leading to electron detachment (collisional detachment and associative detachment) can also be rigorously treated in this formalism.[47,68–70]

The methods we have employed in the calculations on H_2^- extend the Stieltjes-moment approach of Hazi and co-workers[29–31,45] to the calculation of $\Gamma(E,R)$. In particular, we also obtain information on the background scattering and on the angular distribution of both resonant and background scattering. The knowledge of the background T matrix and eigenphases is important for broad resonances, such as the ${}^2\Sigma_u^+$ resonance in e-H_2 scattering, for s-wave scattering phenomena such as virtual states[71,72] and for resonances in polar molecules where the background phase shift may exhibit rapid variations at low energy caused by the long-range dipole potential.[73,74]

Finally, we mention that the present results resolve the question raised by Nesbet[22] of whether a potential-energy curve of the ${}^2\Sigma_u^+$ state of H_2^- can be unambiguously defined at all. The difficulty in defining a meaningful potential-energy curve arises from the large width of the resonance at near-equilibrium internuclear distances. However, a potential-energy curve $E_{\text{res}}(R)$, which joins continuously and with continuous derivative to the bound state of H_2^-, is given by the pole of the resonant K matrix, defined via[61]

$$\delta_{\text{res}}^{\text{sum}}(E_{\text{res}})=\pi/2 \tag{37}$$

which leads to the implicit equation (36) for the resonance position E_{res}. Since the level shift Δ is large, this potential-energy curve differs considerably from the potential-energy curve $\epsilon_d(R)$ of the discrete state given by the stabilization calculation. The resonance energy as defined by Eq. (37) depends, of course, on the separation of the eigenphase sum into a resonant and a background term [the full eigenphase sum, for example, often never reaches $\pi/2$ and Eq. (37) would have no solution when applied to the full eigenphase sum]. Having obtained a physically meaningful separation of the eigenphase sum, we have thus also constructed a well-defined potential-energy curve of the ${}^2\Sigma_u^+$ state of H_2^-. The potential-energy curve of H_2^- will be discussed in more detail in a later paper dealing with the nuclear dynamics in e-H_2 scattering.[68]

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