

## Direct calculation of complex resonance poles using separable expansions of the potential: Application to the ${}^2\Sigma_u^+$ shape resonance in electron- $\text{H}_2$ scattering

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We present a novel scheme to calculate directly the complex resonance poles in electron-atom or electron-molecule scattering. The method is based on the many-body Green's-function formalism and the use of separable expansions of the self-energy part. It is shown that the poles are given by the complex zeros of certain determinants, which can be straightforwardly calculated using analytically determined matrix elements of the free-particle Green's function. We introduce a projection procedure which (i) leads to a simple and unified description of shape resonances as quasiparticles and (ii) is essential for the numerical feasibility of the calculations. Exploratory calculations are performed for the  ${}^2\Sigma_u^+$  shape resonance in electron- $\text{H}_2$  scattering in the static-exchange approximation. This resonance represents a difficult problem owing to its large width at short and intermediate internuclear distances. The fundamental difficulties which arise when using basis-set representations of the potential in the calculation of complex resonance poles are discussed.

### I. INTRODUCTION

The calculation of the complex poles of the  $S$  matrix,  $T$  matrix, or Green's function is of considerable current interest as a means of characterizing resonances in electron-atom and electron-molecule scattering. A well-known method for determining directly the complex poles was formulated by Siegert<sup>1</sup> and applied more recently to a variety of problems, see, e.g., Refs. 2–5. An alternative approach is the method of complex-coordinate rotation<sup>6–9</sup> where the resonance poles are obtained as eigenvalues of a dilatation-transformed non-Hermitian Hamiltonian. A modification of this approach is based on the use of a Hermitian Hamiltonian, but with complex basis functions, in variational calculations.<sup>10,11</sup> In addition to numerous calculations for resonances in electron-atom scattering (for a review, see Refs. 9 and 11), *ab initio* calculations of resonance poles in electron-molecule scattering are now becoming available.<sup>12–15</sup> It is generally found that the inclusion of polarization and correlation effects is important to obtain accurate resonance energies and widths. So far, self-consistent field (SCF) and configuration-interaction (CI) techniques have been implemented for the direct calculation of molecular resonance poles.<sup>12,13,15</sup>

An alternative approach to the correlation and polarization problem is based on the many-body Green's-function formalism.<sup>16</sup> It can be shown that the complex poles of the single-particle Green's function for an  $N$ -electron system determine the resonances in electron scattering from this system and also contain information on the unstable states of the  $(N-1)$ -electron system.<sup>17,18</sup> The many-body Green's-function approach has been used in combination with Siegert-state techniques<sup>19</sup> and complex-coordinate techniques<sup>20–22</sup> to calculate shape resonances in electron-atom scattering and atomic Auger resonances.<sup>21,23–25</sup> A particular advantage of the perturbation-theoretic Green's

function approach is the balanced treatment of correlation in the  $N$ - and  $(N\pm 1)$ -electron systems, which has been amply demonstrated by the calculation of ionization potentials and electron affinities.<sup>26,27</sup>

Another important aspect of a consistent use of Green's functions is that—in contrast to all standard methods of quantum chemistry—the electronic kinetic-energy operator is not approximated by a representation in a finite basis. In the present work we exploit this particular feature of the Green's-function approach. Employing separable expansions<sup>28,29</sup> of the scattering potential and using analytically calculated matrix elements of the free-particle Green's function, the complex resonance poles can be straightforwardly calculated. The approach is closely related to the Schwinger variational principle for the calculation of resonance poles as discussed by Domcke<sup>30</sup> and Watson<sup>31</sup> and yields the *exact* poles of the Green's function for the approximate separable potential.

An important ingredient for the practical feasibility of the method for electron-molecule scattering resonances is the implementation of the Feshbach projection-operator approach.<sup>32–34</sup> Out of the infinite number of complex poles of the  $S$  matrix, the projection procedure selects one or a few poles which are associated with a given resonance. A first application of this approach to the  ${}^2\Pi_g$  state of  $\text{N}_2^-$  using a self-energy given by the two-particle-hole Tamm-Dancoff approximation (2ph-TDA) has been reported recently.<sup>35</sup> In the present paper we give a more detailed description of the method and apply it, as another test of its performance, to the  ${}^2\Sigma_u^+$  shape resonance in  $e\text{-H}_2$  scattering in the static-exchange approximation.

The complex  $S$ -matrix pole corresponding to the  ${}^2\Sigma_u^+$  ground state of  $\text{H}_2^-$  has first been calculated by Bardsley *et al.*<sup>2</sup> using Siegert-state techniques. The inaccuracies inherent in these early calculations were considerable, however, and only a qualitative picture of the complex ener-

gies of the  ${}^2\Sigma_u^+$  and  ${}^2\Sigma_g^+$  states of  $\text{H}_2^-$  could be obtained. More recently, the complex energy of the  ${}^2\Sigma_u^+$  state at the equilibrium geometry of  $\text{H}_2$  has been calculated by Moiseyev and Corcoran<sup>12</sup> using CI techniques for the dilatation-transformed Hamiltonian. McCurdy and Mowrey<sup>15</sup> have calculated the complex  ${}^2\Sigma_u^+$  pole of  $\text{H}_2^-$  for a range of internuclear distances between 1.4 and 4.0 a.u. using the complex SCF method.<sup>13</sup> Their result at the equilibrium distance of  $\text{H}_2$  is, however, in disagreement with the complex CI estimate of Ref. 12. Since target correlation effects, which are neglected in complex SCF, are not expected to significantly affect the position and width of the  ${}^2\Sigma_u^+$  resonance, this discrepancy illustrates that the unambiguous location of complex poles associated with short-lived molecular shape resonances is not a straightforward task, even for few-electron systems.

## II. OUTLINE OF THE THEORY

### A. Poles of the Green's function for separable potentials

As is well known, resonances in potential scattering can be mathematically described by poles of the analytically continued  $S$  matrix,  $T$  matrix, or Green's function (GF) on the unphysical sheet of the complex energy plane, which corresponds to the lower half of the complex momentum plane.<sup>36</sup> Only those poles which are situated sufficiently close to the real energy axis lead to detectable structures in the scattering cross section and are considered to be of physical relevance.

When dealing with electron-atom or electron-molecule scattering (we confine ourselves to the fixed-nuclei limit throughout this paper), we are faced with the considerable difficulty of the many-body problem, i.e., we have to include the important effects of polarization and excitation of the electronic target system. An elegant way of dealing with the correlation problem in *elastic* electron scattering is provided by the many-body GF formalism.<sup>16</sup> It can be shown that the  $S$  or  $T$  matrices for elastic scattering can be expressed in terms of certain GF's.<sup>37-40</sup> Resonances, in particular, are given by the poles of the analytically continued single-particle GF.<sup>17-25,41,42</sup>

To calculate the GF, one usually starts from the Dyson equation, which has the formal structure<sup>16</sup>

$$G = \tilde{G}_0 + \tilde{G}_0 \Sigma G . \quad (1)$$

Here  $G$  is the exact single-particle GF, while  $\tilde{G}_0$  is the GF calculated with a suitable zero-order Hamiltonian, usually the Hartree-Fock (HF) [also called static-exchange (SE)] Hamiltonian.  $\Sigma$  is the energy-dependent and nonlocal dynamic self-energy which accounts for all effects not included in the SE approximation. Equivalently, Eq. (1) may be written as

$$G = G_0 + G_0 V G , \quad (2)$$

where  $G_0$  is the GF describing propagation of a free particle and  $V$  is the full scattering potential, including the SE potential  $V_{\text{SE}}$ :

$$V = V_{\text{SE}} + \Sigma . \quad (3)$$

The potential  $V$ , which is the effective potential for elastic scattering from a many-body target system, is often called the "optical" potential.<sup>37-40</sup>

The self-energy  $\Sigma$  is defined by a diagrammatic perturbation expansion in terms of the residual electron-electron interaction.<sup>16</sup> It can be shown that the exact  $\Sigma$  can be written as<sup>16,43</sup>

$$\Sigma = \Sigma(\infty) + M^{\text{I}}(E) + M^{\text{II}}(E) , \quad (4)$$

where  $\Sigma(\infty)$  is the energy-independent or static part of the self-energy. The matrix elements of the dynamic parts  $M^{\text{I,II}}(E)$  have the spectral representation<sup>43</sup> (in an arbitrary complete and orthonormal single-particle basis)

$$M_{pq}^{\text{I,II}}(E) = \int_n \frac{m_p^{(n)}(m_q^{(n)})^*}{E - E_n \pm i\eta} , \quad (5)$$

where the summation includes integration over the continuous part of the spectrum and  $\eta$  is the usual positive infinitesimal (the plus sign corresponds to the superscript I, the minus sign to II). It is seen that  $M^{\text{I,II}}(E)$  has poles infinitesimally above or below the real axis as well as cuts extending from the excitation or double-ionization thresholds to  $\pm\infty$ .

The problem of determining the poles of  $G$  has thus been reduced to two independent problems, namely, (i) the construction of suitable approximations for  $\Sigma$  and (ii) the solution of the integral equations (1) or (2). In the present work we address ourselves to problem (ii) and refer the reader interested in topic (i) to the literature, where extensive reviews can be found.<sup>44-48</sup> Our approach to solve Eq. (1) or (2) is to introduce well-known separable expansions<sup>28,29,49</sup> of the potentials  $\Sigma$  or  $V$ , which reduce the integral equations to systems of linear algebraic equations. The more powerful approach is obviously the separable approximation of  $\Sigma$ , since the SE potential  $V_{\text{SE}}$  is then included exactly in the GF  $\tilde{G}_0$  in Eq. (1). However, the calculation of the static-exchange GF is already a formidable computational problem for molecular targets owing to the anisotropy of the static potential and the nonlocality of the exchange potential. For this reason we will consider in the following separable expansions of the full potential  $V$  in Eq. (2), with the result that only matrix elements of the free GF  $G_0$  are required, which can be calculated analytically for suitably chosen basis functions.

Given a set of  $N$  square-integrable orthonormal basis functions, the simplest separable approximation for the potential operator  $V$  is the "truncated" potential<sup>50</sup>

$$V^{(t)} = \sum_{i,j=1}^N |\chi_i\rangle V_{ij} \langle \chi_j| , \quad (6a)$$

$$V_{ij} = \langle \chi_i | V | \chi_j \rangle , \quad (6b)$$

Inserting (6) into (2) and taking matrix elements, we obtain

$$\underline{G} = \underline{G}_0 + \underline{G}_0 \underline{V} \underline{G} , \quad (7)$$

where all quantities  $\underline{X}$  are now  $N \times N$  matrices with matrix elements  $X_{ij} = \langle \chi_i | X | \chi_j \rangle$ . Solving for  $\underline{G}$ , we have

$$\underline{G} = (\underline{1} - \underline{G}_0 \underline{V})^{-1} \underline{G}_0 . \quad (8)$$

It follows that the exact poles of the GF for the approximate potential (6) are given by

$$A(z) \equiv \det[\mathbf{1} - \underline{G}_0(z)\underline{V}(z)] = 0, \quad (9)$$

where  $z$  is the complex energy variable. We have made explicit that the energy dependence of  $A$  results both from the free GF and from the energy dependence of the optical potential as shown in Eqs. (4) and (5).

An alternative well-known separable expansion of the potential is<sup>28,29,49</sup>

$$V^{(s)} = \sum_{i,j=1}^N V |\chi_i\rangle \langle V^{-1} \rangle_{ij} \langle \chi_j | V. \quad (10)$$

An elementary calculation gives the following explicit expression for the GF:

$$G = G_0 + \sum_{i,j=1}^N G_0 V |\chi_i\rangle \langle N^{-1} \rangle_{ij} \langle \chi_j | V G_0, \quad (11a)$$

$$N_{ij} = \langle \chi_i | (V - V G_0 V) | \chi_j \rangle. \quad (11b)$$

It follows that the exact poles of the GF for the approximate potential (10) are given by

$$B(z) \equiv \det \underline{N}(z) = 0. \quad (12)$$

As before, the  $z$  dependence of  $\underline{N}$  results from the energy dependence of the free GF  $G_0$  as well as from the optical potential  $V$ . It should be noted that Eq. (11) for the GF is equivalent to the Schwinger variational principle for the  $T$  matrix.<sup>28,29,49</sup>

The calculation of complex resonance poles has thus been reduced to the determination of zeros of the complex functions  $A(z)$  or  $B(z)$ . It has been shown for the simple case of single-channel or multichannel scattering from a square-well potential that the expansion (10) is very efficient, i.e., that accurate estimates of the poles are obtained with few basis functions.<sup>30,31</sup>

Electron-molecule scattering is, of course, a significantly more difficult problem. To apply the method, matrix elements of the operators  $V$ ,  $G_0$ , and  $V G_0 V$  are required. Choosing, as is usual in molecular applications, Cartesian Gaussian functions as atomic basis functions, the matrix elements of  $V$  can be obtained using standard bound-state electronic-structure codes. The matrix elements of the free-particle GF

$$\langle \chi_i | G_0(k) | \chi_j \rangle = 2 \int d^3q \frac{\langle \chi_i | \mathbf{q} \rangle \langle \mathbf{q} | \chi_j \rangle}{k^2 - q^2},$$

where  $k$  is the complex momentum variable and  $\langle \mathbf{r} | \mathbf{q} \rangle$  is a plane wave with momentum  $\mathbf{q}$ , can be calculated analytically for Gaussian basis functions. The formulas for matrix elements involving Cartesian Gaussian functions up to  $f$ -type symmetry have been collected in Ref. 51 for real positive  $k$ . Since all matrix elements of  $G_0$  with Gaussians are entire analytic functions of  $k$ , the analytic continuation into the whole  $k$  plane is straightforward. More details are given in the Appendix. Matrix elements of the operator  $V G_0 V$ , which are required when the Schwinger-type expansion (10) is to be used, are more difficult to calculate. In practice, one may simplify this problem by inserting a large "quadrature basis" between the operators  $V$

and  $G_0$ , with the result that only matrix elements of  $V$  and  $G_0$  are needed.<sup>52</sup>

It should be stressed that all approximations introduced so far affect only the potential operator  $V$ . The kinetic-energy operator  $K = -\frac{1}{2}\nabla^2$  of the scattered electron is never approximated in a basis, but is included exactly via the analytically calculated matrix elements of the free Green's function.

Accurate calculations of electron-molecule scattering resonances require the use of large basis sets including diffuse functions to obtain a sufficiently good representation of the scattering potential. When large basis sets are used, however, a serious numerical difficulty arises in actual calculations. The modulus of the determinants  $A(z)$  or  $B(z)$  becomes exceedingly small, which renders the determination of zeros extremely cumbersome. For this reason the calculation of resonance poles via the zeros of  $A(z)$  or  $B(z)$  is not a practical scheme for actual calculations. We have found a simple and efficient resolution of this problem using projection techniques, which are described in the next subsection.

### B. Projection-operator formalism for the poles of the Green's function

Let us assume that we are interested in the description of an isolated shape resonance. The extension of the formalism to describe several overlapping resonances and/or core-excited resonances is straightforward. We postulate the existence of a square-integrable single-particle wave function  $\phi_d(\mathbf{r})$  which approximately describes the resonance. In actual calculations,  $\phi_d(\mathbf{r})$  may be constructed using either the stabilization method<sup>53,54</sup> or the minimum-variance method.<sup>55,56</sup>

Given the discrete state  $|\phi_d\rangle$ , we may define projectors in the single-particle Hilbert space according to

$$Q = |\phi_d\rangle \langle \phi_d|, \quad P = 1 - Q. \quad (13)$$

Using well-known projection-operator techniques,<sup>32,57</sup> the GF describing propagation in the one-dimensional  $Q$  space may be written as

$$G_{dd}(z) \equiv \langle \phi_d | G(z) | \phi_d \rangle = [z - H_{dd}(z)]^{-1} \quad (14)$$

with

$$H_{dd}(z) = \epsilon_d(z) + F(z), \quad (15)$$

$$\epsilon_d(z) = \langle \phi_d | H(z) | \phi_d \rangle = \epsilon_d^{(0)} + \langle \phi_d | \Sigma(z) | \phi_d \rangle, \quad (16)$$

$$F(z) = \langle \phi_d | H(z) \hat{G}(z) H(z) | \phi_d \rangle, \quad (17)$$

$$H(z) = -\frac{1}{2}\nabla^2 + V(z). \quad (18)$$

Here  $H_{dd}(z)$  is the effective Hamiltonian in  $Q$  space which takes account of the coupling to the  $P$  space via the complex level-shift function  $F(z)$ .  $\epsilon_d^{(0)} = \langle \phi_d | (K + V_{SE}) | \phi_d \rangle$  is the static-exchange orbital energy of the discrete state  $|\phi_d\rangle$ . The GF  $\hat{G}(z)$  in Eq. (17) is the full GF projected onto  $P$  space. It can be constructed by solving

$$\hat{G} = \hat{G}_0 + \hat{G}_0 V \hat{G}, \quad (19)$$

where  $\hat{G}_0$  is the free-particle GF in  $P$  space, which is explicitly given by<sup>33,58,59</sup>

$$\hat{G}_0 = G_0 - G_0 |\phi_d\rangle \langle \phi_d| G_0 |\phi_d\rangle^{-1} \langle \phi_d| G_0. \quad (20)$$

It follows from Eqs. (14) and (15) that the poles of  $G$  in the complex energy plane which appear with nonzero residue in  $G_{dd}(z)$  are given by

$$D(z) \equiv G_{dd}(z)^{-1} = z - \epsilon_d(z) - F(z) = 0. \quad (21)$$

It is clear from Eqs. (17)–(20) that the calculation of the level-shift function  $F(z)$  is not easier than the calculation of matrix elements of  $G$ . In practice, Eq. (19) has to be solved using separable expansions of  $V$  as discussed in the preceding section. Clearly, the zeros of  $D(z)$  are identical with the zeros of  $A(z)$  or  $B(z)$  if the corresponding separable expansions are used in Eq. (19). The advantage gained by introducing  $G_{dd}(z)$  becomes more apparent, however, when we consider the biorthogonal expansion of  $G$  (Ref. 18)

$$G(z) = \sum_{\nu} \frac{|\Psi_{\nu}\rangle \langle \bar{\Psi}_{\nu}|}{z - z_{\nu}}, \quad (22)$$

where the summation is over all poles  $z_{\nu}$  of  $G(z)$ , which are the solutions of Eq. (21). It follows that

$$G_{dd}(z) = \sum_{\nu} \frac{R_{\nu}}{z - z_{\nu}}, \quad (23)$$

$$R_{\nu} = \langle \phi_d | \Psi_{\nu} \rangle \langle \bar{\Psi}_{\nu} | \phi_d \rangle. \quad (24)$$

The residues of the poles of  $G_{dd}$  are thus determined by the overlap of the discrete state  $|\phi_d\rangle$  with the “resonance wave functions”  $|\Psi_{\nu}\rangle$ . The  $|\Psi_{\nu}\rangle$  are the well-known Siegert states,<sup>1</sup> satisfying

$$(H - z_{\nu}) |\Psi_{\nu}\rangle = 0$$

for the complex energy  $z_{\nu} = k_{\nu}^2/2$  with the outgoing-wave boundary condition

$$\Psi_{\nu}(r) \sim e^{ik_{\nu}r}$$

for  $r \rightarrow \infty$ . If  $|\phi_d\rangle$  is a good approximation to a given isolated resonance, only one of the overlaps  $\langle \phi_d | \Psi_{\nu} \rangle$  will be significant, all others being very small. The modulus of the residue  $R_{\nu}$  thus gives a very useful indication of the character of a given pole  $z_{\nu}$ . There is no need to construct the states  $|\Psi_{\nu}\rangle, |\bar{\Psi}_{\nu}\rangle$  explicitly, since the residue may be obtained directly from Eq. (14) by expanding  $H_{dd}(z)$  about the pole  $z_{\nu}$ , giving

$$R_{\nu} = [1 - \epsilon'_d(z_{\nu}) - F'(z_{\nu})]^{-1}, \quad (25)$$

where the prime indicates differentiation with respect to  $z$ . For bound-state poles,  $R_{\nu}$  is real, positive, and smaller than unity. For complex resonance poles,  $R_{\nu}$  is complex, and its modulus is not bounded.

The projection formalism outlined above provides the basis for a unified description of shape resonances in electron-molecule scattering as “quasiparticles,” a concept which is well established in condensed-matter physics.<sup>16–18</sup> The present description includes the effects of electron correlation [represented by the dynamic self-

energy  $\Sigma(z)$ ] and discrete-continuum coupling [represented by the complex level shift  $F(z)$ ] on an equal footing. If the dynamical self-energy  $\Sigma(z)$  and the level shift  $F(z)$  are small and smooth functions of energy for  $z \approx \epsilon_d^{(0)}$ , Eq. (21) will have a solution  $z_0$  close to  $\epsilon_d^{(0)}$  with a residue  $|R_0|$  close to unity. This solution represents a narrow resonance, or, in other words, a well-defined quasiparticle. If either  $\Sigma(z)$  or  $F(z)$  are large and strongly energy dependent in the vicinity of  $\epsilon_d^{(0)}$ , Eq. (21) will no longer have a single solution with a large residue. Rather, we will find several solutions  $z_{\nu}$  with comparable residues  $|R_{\nu}|$ , none of which can be identified as a quasiparticle occupying the discrete orbital  $\phi_d(r)$ .

The above considerations also have important implications for practical calculations. In contrast to the determinants  $A(z)$  and  $B(z)$  of Eqs. (9) and (12), which become exceedingly small when large basis sets are used, the function  $D(z)$  of Eq. (21) is numerically well-behaved in the vicinity of  $\epsilon_d^{(0)}$  and its zeros are easily located. The reason is that  $G_{dd}(z) = D(z)^{-1}$  has only one or a few poles with large residues, the remaining infinitely many poles being strongly suppressed by the projection onto the discrete state  $|\phi_d\rangle$ . It is also interesting to note that  $D(z)$  is a *meromorphic* function with an infinite number of poles on the unphysical sheet, while the determinants  $A(z), B(z)$  are *entire* analytic functions on both sheets.

### III. CALCULATIONS FOR THE ${}^2\Sigma_u^+$ SHAPE RESONANCE IN ELECTRON- $H_2$ SCATTERING

We have applied the above-described formalism to calculate the complex pole corresponding to the well-known  ${}^2\Sigma_u^+$  shape resonance in  $e$ - $H_2$  scattering as a function of the internuclear distance  $R$ . This pole has been the subject of an early study of Bardsley *et al.*<sup>2</sup> and of more recent complex SCF and complex CI calculations by McCurdy and Mowrey<sup>15</sup> and Moiseyev and Corcoran.<sup>12</sup> We have performed calculations both on the SE level of approximation as well as with the 2ph-TDA optical potential.<sup>44,47</sup> It turns out that polarization and correlation effects are not of major importance for the description of the  ${}^2\Sigma_u^+$  resonance of  $H_2$ . The more interesting aspects of the problem arise from the large width of the  ${}^2\Sigma_u^+$  resonance of  $H_2$  at short internuclear distances. Therefore we confine ourselves to a discussion of the SE results. We emphasize, however, that the inclusion of correlation and polarization effects is important for almost all other molecules (see, e.g., Ref. 35).

Calculations have been performed for nine internuclear distances ranging from  $R = 1.4014$  a.u. [the equilibrium distance of  $H_2$  (Ref. 60)] to  $R = 3.0$  a.u. For each internuclear distance a HF calculation for the  $X^1\Sigma_g^+$  ground state of  $H_2$  has been performed using the  $10s5p1d$  uncontracted Gaussian basis set of Schulman and Kaufmann.<sup>61</sup> The basis functions and their exponents are specified in Table I. Schulman and Kaufman have demonstrated the approximate completeness of this single-particle basis by testing various sum rules.<sup>61</sup> The  $s, p_z,$  and  $d_{zz}$  functions of this basis form the “scattering basis set”  $\{\langle \mathbf{r} | \chi_i \rangle\}$  in the  ${}^2\Sigma_u^+$  symmetry which defines the truncated potential

TABLE I. Gaussian basis set for  $e\text{-H}_2$  scattering. Exponents of the basis functions on the atoms are listed.

$s$	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

operator  $V^{(t)}$  according to Eq. (6). Since the basis orbitals are nonorthogonal, the overlap integrals have to be explicitly taken into account in the actual calculations.

Once the scattering potential is defined, we construct a suitable discrete state  $\phi_d(\mathbf{r})$ . Employing the well-known stabilization method,<sup>53,54</sup> we have diagonalized the SE Hamiltonian  $H_{SE} = K + V_{SE}$  in discrete Gaussian basis sets of various sizes, looking for approximately stable eigenvalues of  $\sigma_u$  symmetry. It is found that after the removal of the three most diffuse  $s$  orbitals of the HF basis the energy of the lowest unoccupied  $\sigma_u$  orbital becomes approximately stable with respect to further restrictions of the basis. Removal of  $p$ -type functions had no significant effect on the  $\sigma_u$  orbital energy. The discrete state was thus taken as the lowest unoccupied  $\sigma_u$  orbital in this restricted basis. It has been shown in Ref. 62 that the projection defined by this particular discrete state leads to a clean and physically sensible separation of the  ${}^2\Sigma_u^+$  eigenphase sum into a smooth background term and resonant term which varies rapidly with respect to energy and internuclear distance. It can be seen from Ref. 62 that  $Q = |\phi_d\rangle\langle\phi_d|$  is a suitable projector even for near-equilibrium distances where the  ${}^2\Sigma_u^+$  resonance is very broad.

Given the discrete state, the complex level-shift function  $F(z)$  is calculated from Eq. (17). The background GF  $\hat{G}(z)$  is constructed by solving Eq. (19) using the separable potential (6). Finally, the complex zeros of  $D(z)$  defined in Eq. (21) are located using a search routine based on Muller's method.<sup>63</sup> Provided that a reasonably accurate starting guess is available, the zero of  $D(z)$  can be converged to eight digits with four to ten iterations, depending on the residue of the pole. For each final pole  $z_\nu$  the residue  $R_\nu$  defined in Eq. (25) has been computed by numerical differentiation.

The results obtained in this manner are collected in Table II. The table shows the poles (in electron volts) and their residues in the lower half of the unphysical sheet of the complex energy plane (corresponding to the fourth quadrant of the complex momentum plane). Each pole has a mirror image in the upper half of the energy plane (corresponding to the third quadrant of the  $k$  plane).<sup>36</sup>

Let us first consider the larger internuclear distances where the  ${}^2\Sigma_u^+$  resonance is narrow. At  $R = 3.0$  a.u. we find a pole very close to the origin of the complex energy plane. This is consistent with several other calculations which predict a crossing of the  ${}^2\Sigma_u^+$  potential of  $\text{H}_2^-$  and the  ${}^1\Sigma_g^+$  potential of  $\text{H}_2$  close to 3.0 a.u.<sup>2,15,64,65</sup> Beyond about 3.0 a.u. the  ${}^2\Sigma_u^+$  state of  $\text{H}_2^-$  is bound with respect to electron detachment and its energy and wave function can be accurately calculated using standard methods of quantum chemistry.<sup>64-66</sup> When the internuclear distance

is reduced, the pole moves out into the complex plane as expected for a  $p$ -wave shape resonance, i.e., the width increases as the 1.5th power of the resonance energy near threshold.<sup>36,67</sup>

It is seen from Table II that the pole (called  $z_1$  in Table II) recedes rapidly from the real axis with decreasing internuclear distance. At  $R = 2.0$  a.u. the imaginary part of the complex energy is of about the same size as the real part. When  $R$  is further reduced, it is found that the search procedure locating the zeros of  $D(z)$  converges systematically to another pole (called  $z_2$  in Table II) which is not adiabatically connected with  $z_1$ . Only after the factor  $z - z_2$  is divided out does the search procedure converge to the adiabatic continuation of  $z_1$ . The origin of this behavior is obvious when considering the residues  $|R_1|$  and  $|R_2|$  in Table II. At  $R \approx 2.0$  a.u. the residue  $|R_1|$  drops from a value close to unity to a small value, while the pole  $z_2$  attains a large residue. According to the discussion in the preceding section, we have to conclude that the  ${}^2\Sigma_u^+$  resonance is represented by the pole  $z_2$  for  $R \lesssim 2$  a.u., while  $z_1$  is the relevant pole for  $R \gtrsim 2$  a.u. For  $R \approx 3$  a.u., where the pole  $z_1$  becomes a bound state, the pole  $z_2$  has a small residue and is too far from the real axis to have observable consequences.

To give also a visual representation of the results, we show in Fig. 1(c) the trajectories of the poles  $z_1$  and  $z_2$  in the complex momentum plane [Figs. 1(a), 1(b), and 1(d) will be discussed below]. The calculated poles are shown as circles; to guide the eye, those poles which belong to a trajectory are connected by straight lines. The poles move towards the origin with increasing internuclear distance. Note that the disconnected set of poles in Fig. 1(c) represents the trajectory of the pole  $z_2$  and is not a continuation of the trajectory of  $z_1$ . As can be seen from Table II, the residue "jumps" from  $z_2$  to  $z_1$  when the internuclear distance increases beyond  $\approx 2$  a.u.

The present results as shown in Table II and Fig. 1(c) are clearly at variance with the results of McCurdy and Mowrey<sup>15</sup> obtained by the complex SCF method. McCurdy and Mowrey found a single complex pole which represents the  ${}^2\Sigma_u^+$  resonance for the whole range of internuclear distances between 1.4 and 3.0 a.u. This poses the question of whether the "splitting" of the pole trajectory observed in the present calculations is an artifact of the representation of the potential operator in a basis (which is, apart from the SE approximation, the only approximation in our calculations). We have performed, therefore, a series of test calculations, varying the size of the scattering basis which defines the truncated scattering potential according to Eq. (6).

The simplest test is to reduce the size of the scattering basis by removing successively the most diffuse basis

TABLE II. Poles  $z_n$  in the lower half of the complex energy plane (real and imaginary parts are given in eV) and their residues  $|R_n|$  for the  ${}^2\Sigma_u^+$  symmetry of  $H_2^-$  at nine internuclear distances between 1.4014 and 3.0 a.u. obtained with the truncated potential (6) using the scattering basis given in Table I. Corresponding trajectories in the complex momentum plane are shown in Fig. 1(c). At  $R = 3.0$  a.u., where the pole  $z_1$  is located very close to threshold, the differentiation of  $F(z)$  was found to be numerically unstable and the residue  $R_1$  could not be determined.

	1.4014	1.6	1.8	2.0	2.2	2.4	2.5	2.75	3.0
$z_1$	1.255, -1.556	1.313, -1.376	1.325, -1.214	1.299, -1.020	1.193, -0.786	0.962, -0.542	0.820, -0.437	0.375, -0.188	0.024, -0.0026
$ R_1 $	0.28	0.31	0.40	0.52	0.67	0.78	0.82	0.89	
$z_2$	4.391, -3.376	4.137, -2.638	3.707, -2.391	3.247, -2.206	2.807, -2.159	2.462, -2.180	2.329, -2.189	2.084, -2.176	1.916, -2.144
$ R_2 $	1.22	1.09	1.02	0.91	0.74	0.53	0.44	0.29	0.20

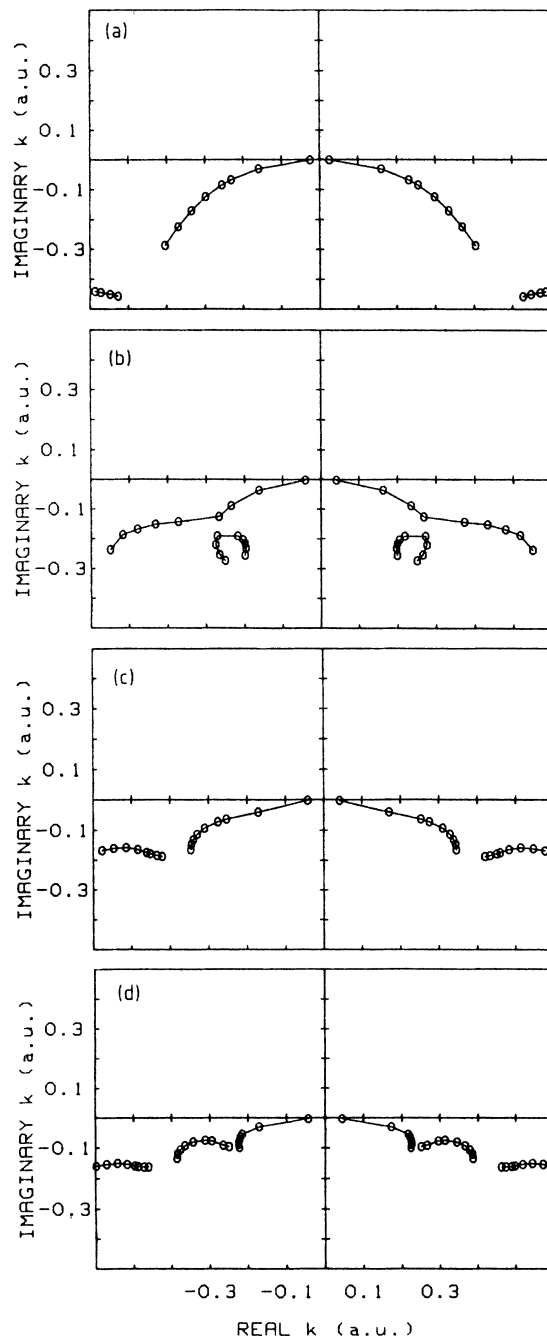


FIG. 1. Poles of the GF in the complex momentum plane corresponding to the  ${}^2\Sigma_u^+$  shape resonance in  $e$ - $H_2$  scattering in the SE approximation obtained with various scattering basis sets. Results obtained with the reference basis set given in Table I are shown in (c); (b) and (a) show the results obtained after the removal of one or two diffuse  $s$  functions, respectively. (d) shows the results obtained by including two additional very diffuse  $s$  functions in the quadrature set. Poles which are connected by lines are parts of a pole trajectory, i.e., these poles are transformed into each other by changing the internuclear distance. (a)–(c) show the trajectories of two poles, whereas three poles are present in (d). Poles generally move towards the origin with increasing internuclear distance; an obvious exception is seen in (b) where one of the poles describes a nearly circular trajectory.

functions. We have performed calculations by removing (i) the  $d_{zz}$  function, (ii) one or two of the  $p_z$  functions, and (iii) one or two of the  $s$  functions from the scattering basis. It turns out that the poles are most sensitive to changes in the set of  $s$ -type functions. Figure 1(a) shows the pole trajectories obtained after the removal of the two most diffuse  $s$  functions from the scattering basis; Fig. 1(b) shows the results obtained after the removal of only one  $s$  function. Figures 1(a)–1(c) thus illustrate the evolution of the pole trajectories with increasing size of the basis of  $s$ -type functions.

The trajectory of Fig. 1(a) moves rapidly into the complex momentum plane with decreasing internuclear distance. Apparently, the potential  $V^{(t)}$  in this reduced basis cannot account properly for the barrier which stabilizes the  ${}^2\Sigma_u^+$  shape resonance. With one more  $s$ -type function added [Fig. 1(b)], the trajectory approaches the real axis, but we observe a distinct perturbation of this trajectory by an unphysical “background pole” which describes an approximately circular trajectory in the complex momentum plane. The comparison of Figs. 1(b) and 1(c) suggests that the splitting of the trajectory of Fig. 1(c) is caused by the presence of this background pole.

It is of course desirable to consider also extensions of the scattering basis set beyond the reference basis given in Table I. To this end we have considered a simple approximation to the Schwinger-type Green’s function of Eq. (11). The difficulty in the evaluation of Eq. (11) is the calculation of the matrix elements of  $V_{SE}G_0(k)V_{SE}$  for complex  $k$ . As pointed out by Watson *et al.*<sup>52</sup>, these matrix elements may be approximately evaluated by inserting a quadrature basis, which is larger than the scattering basis, between the operators  $V_{SE}$  and  $G_0$ . Such a calculation is largely equivalent to a calculation with a truncated potential operator  $V^{(t)}$  defined in a larger basis, namely the quadrature basis. We have performed test calculations with quadrature basis sets obtained by augmenting the scattering basis by diffuse  $s$  or  $p$  functions. Again, the poles are found to be most sensitive to the addition of  $s$ -type functions. The pole trajectories obtained with two additional  $s$  functions with exponents 0.006 and 0.002 are shown in Fig. 1(d). In this case we locate the trajectories of three poles,  $z_1$ ,  $z_2$ , and  $z_3$ . Similar to the case of Fig. 1(c) (see Table II), the residue of the  ${}^2\Sigma_u^+$  resonance is redistributed among these poles with varying internuclear distance. For larger distances ( $R \geq 2.7$  a.u.)  $z_1$  (i.e., the pole closest to the origin) has a large residue; for intermediate distances ( $2.5 \geq R \geq 2.2$  a.u.) the pole  $z_2$  has the dominant residue; for short distances ( $R \leq 2.0$  a.u.), the pole  $z_3$  has the largest residue. It is thus clear that none of the poles  $z_1, z_2, z_3$  alone can represent the  ${}^2\Sigma_u^+$  resonance for all internuclear distances.

#### IV. DISCUSSION

The results presented in the preceding section illustrate that the approximation of the scattering potential in a basis is not a trivial step when calculating the analytic properties of the GF or  $S$  matrix in the complex plane. This question requires, therefore, a detailed discussion. The analytic properties of  $S$  or  $G$  in the lower half of the complex momentum plane (corresponding to the unphysi-

cal sheet of the energy plane) are known to depend sensitively on the long-range behavior of the potential.<sup>36</sup> The truncated potential operator of Eq. (6), for example, represents with our choice of basis functions a nonlocal separable potential with Gaussian form factors in coordinate space. Following the lines of earlier work by Regge<sup>68</sup> and Sartori<sup>69</sup> for local potentials which vanish faster than any exponential for  $r \rightarrow \infty$ , it is straightforward to establish qualitative but rigorous statements about the distribution of the poles in the complex momentum or energy plane. As discussed in the Appendix, all matrix elements of  $G_0$  with Gaussians are entire analytic functions of the complex momentum variable  $k$  and are given in terms of the complex error function. It follows that the determinant  $A(k)$  defined in Eq. (9) is an entire analytic function of order 2 (see, for example, Ref. 70 for the definition of the order of an entire analytic function). As is well known, the order of an entire function determines to a large extent the asymptotic distribution of its zeros. The most important results in the present context are<sup>68,69</sup>

(i)  $A(k)$  has an infinite number of zeros in the complex  $k$  plane,

(ii) if  $\bar{N}(h)$  is the number of zeros  $k_\nu$  of  $A(k)$  with  $|k_\nu| < h$ , then  $\bar{N}(h) = O(h^2)$  for  $h \rightarrow \infty$ .

Numbering the zeros  $k_\nu$  in the order of increasing modulus, it follows from (ii) that

$$|k_{\nu+1} - k_\nu| = O(\nu^{-1/2})$$

for  $\nu \rightarrow \infty$ , i.e., the distance between neighboring zeros in the  $k$  plane vanishes asymptotically. This should be compared with the case of cut-off potentials, i.e.,  $V(r) = 0$  for  $r > a$ , where  $|k_{\nu+1} - k_\nu| = O(1)$  asymptotically.<sup>68</sup> When we map the zeros of  $A(k)$  into the energy plane according to  $z_\nu = k_\nu^2/2$ , we have  $|z_{\nu+1} - z_\nu| = O(1)$  for  $\nu \rightarrow \infty$ . In the energy plane the zeros of  $A(z)$  are thus distributed equidistantly for  $|z| \rightarrow \infty$ .

It should be clear that these properties of the zeros of  $A(k)$  and, thus, of the poles of the GF are a universal feature of separable potentials with Gaussian form factors. The above-discussed distribution of the poles of  $G$  reflects the Gaussian cutoff of the potential in coordinate space, and we may call these pole “cutoff poles.”<sup>5</sup> Since the true scattering potential is not of Gaussian form at large distances, the true GF will exhibit a completely different asymptotic distribution of poles and possibly additional singularities such as branch cuts. When employing basis-set representations of the potential, it is thus important to distinguish between “physical” resonance poles and “unphysical” cutoff poles.

To illustrate this important point more specifically, it is useful to consider, as the simplest case, a rank-one separable potential

$$V = V_0 |f\rangle\langle f|$$

with variable strength parameter  $V_0$ . In this case the poles of  $G(k)$  are simply given by

$$\langle f | G_0^{(+)}(k) | f \rangle = V_0^{-1}.$$

Choosing, for comparison with the  ${}^2\Sigma_u^+$  symmetry of  $H_2^-$ , a  $p$ -wave form factor

$$\langle r | f \rangle = N r e^{-\alpha r^2} \cos \theta,$$

where  $N$  is a normalization constant, the poles of  $G$  are given by the zeros of

$$F(\kappa) = 1 + 2\kappa^2 + 2i\sqrt{\pi}\kappa^3 w(\kappa) + 3\alpha/2V_0,$$

where  $\kappa = k/\sqrt{2\alpha}$  is the dimensionless momentum variable and  $w(z)$  is related to the complex error function (see Appendix).

We have determined numerically the first few zeros of  $F(\kappa)$  [poles of  $G(\kappa)$ ], for varying potential strength  $V_0$ . Figure 2 shows the trajectories of the four poles closest to the origin in the fourth quadrant of the complex  $\kappa$  plane (these zeros have mirror images in the third quadrant). The pole closest to the imaginary axis coalesces with its mirror image at the origin for  $V_0 = -\frac{3}{2}\alpha$ . For  $V_0 < -\frac{3}{2}\alpha$ , a bound-state pole moves up the positive imaginary axis, and a virtual-state pole down the negative imaginary axis. The remaining infinitely many poles (three of which are shown) are seen to cross the bisector  $\arg\kappa = -\pi/4$  with increasing  $|V_0|$  and to approach certain fixed points for  $V_0 \rightarrow -\infty$ . It can be seen that the distance between poles decreases for increasing  $v$ .

The infinitely many poles situated in the vicinity of the bisector  $\arg\kappa = -\pi/4$  are the above-mentioned cutoff poles which reflect the Gaussian decay of the potential in coordinate space. Remembering that  $k = \kappa\sqrt{2\alpha}$ , it is clear that the inclusion of very diffuse basis functions in the representation of the potential will introduce cutoff poles close to the origin of the  $k$  plane.

The numerical convergence studies of Sec. III as well as the above general discussion indicate that the splitting of the pole trajectory of the  ${}^2\Sigma_u^+$  resonance state of  $\text{H}_2^-$  in the present calculations is caused by unphysical cutoff poles which come closer to the real axis as more diffuse basis functions are included in the representation of the potential. For large internuclear distances ( $R = 3.0$  and  $2.75$  a.u. in the present calculations), where the  ${}^2\Sigma_u^+$  resonance is narrow, we obtain converged results with moderate basis sets. For  $R \lesssim 2.5$  a.u., where the reso-

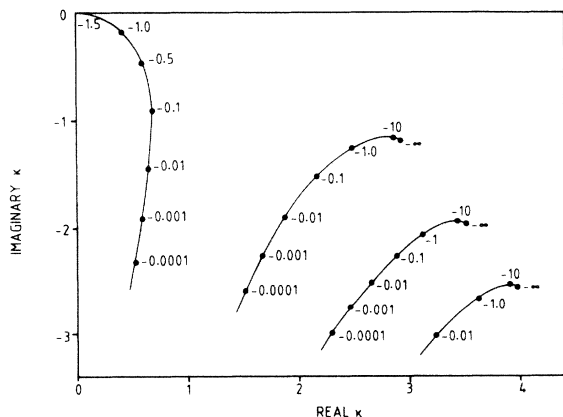


FIG. 2. Pole trajectories in the fourth quadrant of the dimensionless momentum plane for a rank-1 separable potential with  $p$ -wave form factor. Poles have mirror images in the third quadrant. Numbers serve to indicate the movement of the poles with variation of the dimensionless strength parameter  $V_0/\alpha$ .

nance becomes broad, more diffuse basis functions are apparently required for a proper representation of the scattering potential, with the consequence that cutoff poles are introduced closer to the real axis, which then interfere with the physical pole trajectory. We may conclude that calculations based on the truncated potential (6) are not suitable to locate poles associated with very broad shape resonances.

The above model study of a rank-one separable potential indicates a possibility to resolve the problem caused by the cutoff poles. It is seen from Fig. 2 that the location of the cutoff poles is fairly insensitive to the value of the strength parameter  $V_0$ , i.e., the cutoff poles are situated close to the bisector  $\arg\kappa = -\pi/4$  for a wide range of  $V_0$ . It follows that the cutoff poles in the physical  $k$  plane ( $k = \kappa\sqrt{2\alpha}$ ), are rotated away from the real axis by an angle  $\gamma/2$  if we scale the exponent  $\alpha$  of the Gaussian form factor by  $e^{i\gamma}$ . Complex scaling of the basis functions thus appears as a simple means to eliminate the cutoff poles, provided the resonance pole of interest is invariant to the complex scaling. Originally, complex scaling of the basis functions has been introduced to eliminate the spurious poles of the GF on the real axis which appear as a consequence of the truncation of the kinetic-energy operator in an  $L^2$  basis, see, e.g., Refs. 10–13 (these spurious poles are absent in the present approach which avoids any approximations to the kinetic energy). However, the complex scaling may eliminate, in addition, the spurious poles introduced by the basis-set representation of the potential. This explains the single and smooth pole trajectory of the  ${}^2\Sigma_u^+$  resonance of  $\text{H}_2$  obtained by McCurdy and Mowrey with the complex SCF method.<sup>15</sup>

## V. CONCLUSIONS

We have outlined a straightforward scheme which allows the direct calculation of complex resonance poles in electron-atom and electron-molecule scattering. The method is based on the many-body GF formalism and the use of separable expansions of the self-energy operator. The exact GF for the approximate separable potential can be constructed in closed form in the complex momentum or energy plane. To facilitate the location and identification of the poles, a projected GF has been introduced, the residues of which have an immediate interpretation in terms of the overlap of the resonance wave function with a predetermined discrete state. The formalism yields a unified description of shape resonances as quasiparticles which exhibit a finite lifetime and are reduced in strength owing to many-body effects as well as the discrete-continuum coupling. The impact of many-body effects on the resonance energy and width has recently been demonstrated for the  ${}^2\Pi_g$  shape resonance in  $e\text{-N}_2$  scattering.<sup>35</sup> In the present work we have considered the  ${}^2\Sigma_u^+$  shape resonance in  $e\text{-H}_2$  scattering, where many-body effects are of minor importance, but the very short lifetime renders the location of the resonance pole difficult.

The calculations for the  ${}^2\Sigma_u^+$  resonance in  $e\text{-H}_2$  scattering have revealed the limitations of the method [as far as it is based on the truncated potential operator  $V^{(t)}$  of Eq. (6)] for very short-lived resonance states. Since it is well



known that the analytic properties of the  $S$  matrix and the GF in the lower half of the complex momentum plane and far from the real axis are extremely sensitive to the long-range behavior of the scattering potential, it is not surprising that the truncation of the potential in a basis is too crude an approximation for the calculation of broad resonances. More sophisticated versions of the theory may (i) use the Schwinger-type expansion (10) of the potential and (ii) include the static part of the scattering potential in the GF  $G_0$ , treating only the exchange and polarization parts by separable expansions. The practical implementation of such calculations is considerably more difficult, however.

Although the discussion in the present work has concentrated on the limitations of the method based on  $V^{(t)}$  for broad resonances, one should not overlook its attractive features for narrow resonances. The method is straightforwardly applicable to arbitrary polyatomic molecules, and polarization and target correlation are easily included within the many-body GF formalism. The HF calculation, the integral transformation, and the calculation of the poles and residues of  $M(E)$  [see Eq. (5)] have to be done only once for each internuclear distance, which renders the method very efficient and easy to implement. It is also possible to calculate the complex poles corresponding to core-excited or Feshbach resonances which originate from poles of the dynamic self-energy operator  $M(E)$ .

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#### APPENDIX: ANALYTIC CONTINUATION OF THE GREEN'S-FUNCTION MATRIX ELEMENTS

We consider matrix elements of the free-particle Green's function with Cartesian Gaussian basis functions

$$\langle \mu_{lmn}^{\alpha, A} | G_0^{(+)}(k) | \mu_{l'm'n'}^{\beta, B} \rangle = 2(2\pi)^{-3} \int d^3q \frac{\langle \mu_{lmn}^{\alpha, A} | \mathbf{q} \rangle \langle \mathbf{q} | \mu_{l'm'n'}^{\beta, B} \rangle}{k^2 - q^2 + i\eta}, \quad (\text{A1})$$

where

$$G_0^{(+)}(k, \mathbf{r}, \mathbf{r}') = -(2\pi)^{-1} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}, \quad (\text{A2})$$

$$\langle \mathbf{r} | \mu_{lmn}^{\alpha, A} \rangle = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha|\mathbf{r}-\mathbf{A}|^2} \quad (\text{A3})$$

and  $N_{lmn}$  is a normalization factor.<sup>51</sup> As shown by Levin *et al.*,<sup>51</sup> the  $k$  dependence of the matrix elements (A1) is given by integrals of the form

$$I_L^p(k) = - \int_0^\infty dq \frac{q^p e^{-aq^2} j_L(qR)}{k^2 - q^2 + i\eta}, \quad (\text{A4})$$

where  $L$  and  $p$  are integers with  $p \geq L + 2$ ,  $R = |\mathbf{A} - \mathbf{B}|$ ,  $a = (\alpha + \beta)/(4\alpha\beta)$ , and  $j_L$  denotes the spherical Bessel function.<sup>71</sup>

Considering now the  $I_L^p$  as functions of the complex variable  $k = u + iv$ , we evaluate the integral (A4) for values of  $k$  in the first quadrant of the  $k$  plane,  $u > 0$ ,  $v > 0$ . The first quadrant of the  $k$  plane corresponds, via the mapping  $z = k^2/2$ , to the upper half of the physical sheet of the energy plane. The resulting analytic formulas for  $I_L^p(k)$  define the analytic continuation of these matrix elements into the second quadrant of the  $k$  plane (lower half of the physical sheet of the energy plane) as well as to the lower half of the  $k$  plane (unphysical sheet of the energy plane).

The integral  $I_0^2$  can be directly evaluated with the help of integral tables,<sup>72</sup> giving

$$I_0^2(k) = - \frac{\pi}{4R} e^{-ak^2} \left[ e^{ikR} \operatorname{erf} \left[ \frac{R}{2\sqrt{a}} + ik\sqrt{a} \right] + e^{-ikR} \operatorname{erf} \left[ \frac{R}{2\sqrt{a}} - ik\sqrt{a} \right] \right] - i \frac{\pi}{2R} e^{-ak^2} \sin(kR), \quad (\text{A5})$$

where  $\operatorname{erf}(z)$  denotes the error function.<sup>71</sup> All other integrals, such as  $I_0^4$ ,  $I_1^3$ , etc., can be obtained from  $I_0^2$  by differentiation with respect to  $R$  or with the use of the recursion relations of the spherical Bessel functions.<sup>51</sup> Equation (A5) defines, therefore, the analytic continuation of all integrals  $I_L^p(k)$ . In the special case  $R = 0$ , Eq. (A5) reduces to

$$I_0^2(k) = - \frac{1}{2} \sqrt{\pi/a} - i \frac{\pi}{2} kw(k\sqrt{a}), \quad (\text{A6})$$

where

$$w(z) = e^{-z^2} [1 - \operatorname{erf}(-iz)]. \quad (\text{A7})$$

An alternative form of Eq. (A5) is

$$I_0^2(k) = - \frac{\pi}{4R} e^{-R^2/4a} [w(-iz_1) - w(iz_2)] \quad (\text{A8})$$

with

$$z_1 = \frac{R}{2\sqrt{a}} + ik\sqrt{a}, \quad z_2 = \frac{R}{2\sqrt{a}} - ik\sqrt{a}. \quad (\text{A9})$$

In the numerical calculations we have generally used Eq. (A5). On the imaginary  $k$  axis and for small exponents  $\alpha, \beta$  (i.e., large  $a$ ), however, the expression (A5) is numerically ill-behaved, since  $\exp(-ak^2)$  can become exceedingly large. In these cases the alternative form (A8) is numerically stable. Gautschi's algorithm<sup>73</sup> is used to evaluate the complex error function.

The integral  $I_1^3(k)$  can be obtained via

$$I_1^3(k) = - \frac{d}{dR} I_0^2(k) \quad (\text{A10})$$

giving

$$I_1^3(k) = \frac{1}{R} I_0^2(k) + i \frac{\pi}{4R} k e^{-ak^2} \left[ e^{ikR} \operatorname{erf} \left[ \frac{R}{2\sqrt{a}} + ik\sqrt{a} \right] - e^{-ikR} \operatorname{erf} \left[ \frac{R}{2\sqrt{a}} - ik\sqrt{a} \right] \right] \\ + \frac{1}{2R} \left[ \frac{\pi}{a} \right]^{1/2} e^{-R^2/4a} + i \frac{\pi}{2R} k e^{-ak^2} \cos(kR). \quad (\text{A11})$$

An alternative form, analogous to Eq. (A8), is

$$I_1^3(k) = \frac{1}{2R} \left[ \frac{\pi}{a} \right]^{1/2} e^{-R^2/4a} + \left[ \frac{1}{R} + \frac{R}{2a} \right] I_0^2(k) \\ + \frac{\pi}{4R\sqrt{a}} e^{-R^2/4a} [z_1 w(-iz_1) - z_2 w(iz_2)]. \quad (\text{A12})$$

For the special case  $R=0$ , the integral  $I_1^3$  vanishes, as follows immediately from the definition (A4). All remaining integrals  $I_l^2$  follow from  $I_0^2$  and  $I_1^3$  according to the list of formulas given by Levin *et al.*<sup>51</sup> From the integrals  $I_l^2$  the Green's-function matrix elements (A1) are obtained according to Eqs. (15)–(17) of Ref. 51. Thus all matrix elements of the free-particle Green's function are given as entire analytic functions in the  $k$  plane.

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