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Projection-operator calculations for shape resonances: A new method based on the many-body optical-potential approach

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The projection-operator formalism of Feshbach defines a separation of the T matrix into a smooth background term and a resonant T matrix which may vary rapidly with energy. The resonance is characterized by an unperturbed energy ϵ_d, a width function $\Gamma(E)$, and a level-shift function $\Delta(E)$. Such a separation of the fixed-nuclei electron-molecule scattering T matrix is of considerable practical relevance for the treatment of nuclear dynamics in resonant electron-molecule scattering. We present an explicit realization of the projection-operator formalism for electron-molecule scattering within the framework of the many-body optical-potential approach. In contrast to the approach of Hazi [J. Phys. B 11, L259 (1978)] which is based on the use of Stieltjes moment techniques to compute $\Gamma(E)$, we obtain explicitly the background T matrix as well as the information on the angular distribution of the resonant scattering. The performance of the method is illustrated for the well-known 2.3-eV shape resonance in electron scattering from the nitrogen molecule. The two-particle-hole Tamm-Dancoff approximation (2ph-TDA) is adopted for the optical potential and the Schwinger variational principle is used to solve the background scattering problem. The resulting resonance parameters ϵ_d, $\Gamma(E)$, $\Delta(E)$, and the resonant eigenphase sum are in excellent agreement with results obtained previously by Hazi using different computational methods.

I. INTRODUCTION

In recent years there has been increasing interest in the accurate *ab initio* treatment of nuclear dynamics in resonant electron-molecule scattering.[1-5] Of particular interest are reactive electron-molecule collision processes such as dissociative attachment or recombination and the corresponding reverse processes (associative detachment or ionization). These processes violate the Born-Oppenheimer (BO) principle in the sense that electronic energy in converted into kinetic energy of nuclear motion or *vice versa*.

As has been shown by Chen,[6,7] O'Malley,[8] Bardsley,[9,10] and others,[11-14] the projection-operator formalism of Feshbach[15] provides a general and elegant way to formulate the problem. Introducing a projector P, which projects onto the electronic continuum, and a projector Q, which projects onto suitable discrete electronic states embedded in the continuum, one obtains a formal solution of the resonant scattering problem including the dynamics of nuclear motion. The nuclear motion in the electronic resonance state is governed by an energy-dependent, complex, and nonlocal potential.[3-14] The imaginary part of the potential is given by the (nonlocal) decay width of the resonance. The crucial assumptions in this description are that (i) the discrete electronic state is diabatic, i.e., weakly dependent on the nuclear coordinate(s),[16] and (ii) that the nonresonant scattering processes can be treated in the so-called adiabatic-nuclei or impulse approximation.[17,18] The nonlocal width and level-shift operators account for non-BO effects which are important for resonances near threshold,[10,19,20] in particular for polar or charged target molecules.[21,22] To evaluate the nonlocal width and level-shift operators it suffices to know the decay width $\Gamma(E,R)$ of the resonance as a function of the electronic energy E and the internuclear distance(s) R; the level shift $\Delta(E,R)$ is then given by the Hilbert transform of $\Gamma(E,R)$ with respect to E.[3-14]

While the general formalism outlined above has been known for many years, actual calculations based on this formalism have been hindered by two major obstacles, namely, (i) the calculation of the width function $\Gamma(E,R)$, which requires the solution of the fixed-nuclei electron-molecule scattering problem, and (ii) the treatment of nuclear dynamics in the nonlocal complex potential of the resonance state. Progress has been made recently, however, to overcome these computational difficulties. Hazi[23-25] recognized that one need not solve the electron-molecule scattering problem with proper boundary conditions to obtain the width function $\Gamma(E,R)$. Rather, one can use Stieltjes imaging methods to construct a smooth function $\Gamma(E)$ from a discrete representation of the background scattering continuum. This approach is very powerful as it allows the immediate implementation of computational methods for bound states, which have been developed to a high degree of sophistication. Pioneering calculations by Hazi and co-workers[3,4,24-26] have shown that the accurate *ab initio* calculation of $\Gamma(E,R)$ for molecular shape resonances and doubly excited autoionizing states is feasible. The availability of the width and level-shift functions has stimulated new attempts[4,5,27] to solve for the nuclear dynamics in the resonance state without resorting to the usually employed local approximation.[3-13]

In the present work we develop a new method to decompose the fixed-nuclei T matrix for electron scattering (or, equivalently, the eigenphase sum) into a resonant and a background contribution, such that the background term becomes a smooth function of E and R, while rapid variations of the eigenphase sum with E and R are contained in the resonant term. The first step is to reduce the electronic many-body problem to an effective one-body scattering problem using the many-body optical-potential formalism.[28–30] The resulting energy-dependent, nonlocal, and, in general, complex optical potential is given by the irreducible self-energy part of the many-body Green's-function formalism.[28–30] We then apply projection-operator techniques[15] to this effective one-body problem to extract rapid variations of the phase shift due to shape resonances or virtual states. This requires the construction of a suitable (in general, energy-dependent) discrete state, using, for example, the stabilization method.[31,32] In contrast to the approach of Hazi,[23–25] the formalism yields not only the width and level-shift functions needed for the treatment of nuclear dynamics in the resonance state, but also the background T matrix or eigenphase sum. Moreover, because the background scattering problem is solved with proper boundary conditions, we obtain the information on the angular distribution of the resonant and background scattering. To test the performance of the method, we have applied it to the 2.3-eV $^2\Pi_g$ shape resonance in N_2, which is by far the best studied molecular shape resonance, both experimentally and theoretically. In particular, we shall compare our results with the data obtained by Hazi[24,25] using a rather different computational approach. The excellent agreement of the present results with the results of Hazi and experimental data indicate that the systematic *ab initio* calculation of resonance positions and widths to an accuracy of 0.1 eV or better is indeed feasible.

II. OPTICAL-MODEL WAVE FUNCTION

Let us consider the electron-molecule scattering problem in the fixed-nuclei approximation. The many-particle scattering state describing an electron with asymptotic momentum $\vec{k}$ impinging on the molecule in the (correlated) target state $|0\rangle$ reads[33–35]

$$|0,\vec{k}^{(+)}\rangle=\frac{i\eta}{E_0+\epsilon_k-\mathcal{H}+i\eta}a^\dagger_{\vec{k}}\,|0\rangle$$
$$=a^\dagger_{\vec{k}}\,|0\rangle+\frac{1}{E_0+\epsilon_k-\mathcal{H}+i\eta}[V,\,a^\dagger_{\vec{k}}]\,|0\rangle\;, \tag{2.1}$$

where $a^\dagger_{\vec{k}}$ is the creation operator for an electron in the plane-wave state $|\vec{k}\rangle$ with energy $\epsilon_k=k^2/2$, E_0 is the electronic energy of the target molecule, V is the complete interaction part of the Hamiltonian $\mathcal{H}$, and η is the usual positive infinitesimal, which is taken to be zero after all necessary integrations have been performed. The superscript $(+)$ indicates outgoing-wave boundary conditions for the scattered particles. Energy normalized continuum states are assumed throughout. The advantage of the second quantization formalism, on which Eq. (2.1) is based, is that the Pauli principle is satisfied automatically through the anticommutation relations of the fermion creation and annihilation operators.

The complete information on the elastic scattering is contained in the optical-model wave function[28–30]

$$\phi^{(+)}_{\vec{k}}(\vec{r})=\langle 0\,|\,\psi(\vec{r})\,|\,0,\vec{k}^{(+)}\rangle\;, \tag{2.2}$$

where $\psi(\vec{r})$ is the field operator which annihilates an electron at $\vec{r}$. As first shown by Bell and Squires,[28] $\phi^{(+)}_{\vec{k}}(\vec{r})$ can be obtained from the single-particle Green's function of many-body theory.[36] Defining the Green's function in the mixed coordinate-momentum representation

$$G(\vec{r},\vec{k},\omega)=\left\langle 0\left|\psi(\vec{r})\frac{1}{\omega+E_0-\mathcal{H}+i\eta}a^\dagger_{\vec{k}}\right|0\right\rangle$$
$$+\left\langle 0\left|a^\dagger_{\vec{k}}\frac{1}{\omega-E_0+\mathcal{H}-i\eta}\psi(\vec{r})\right|0\right\rangle\;, \tag{2.3}$$

one has[37,38]

$$\phi^{(+)}_{\vec{k}}(r)=\lim_{\gamma\to+0}i\gamma G(\vec{r},\vec{k},\epsilon_k+i\gamma)\;, \tag{2.4}$$

which implies that $G(\vec{r},\vec{k},\omega)$ has a pole at $\omega=\epsilon_k$ with the residue $\phi^{(+)}_{\vec{k}}(\vec{r})$. The infinitesimal $i\gamma$ serves to ensure that we include only causal scattering waves. The Green's function (2.3) obeys the Dyson equation[36]

$$G(\vec{r},\vec{k},\omega)=G_0(\vec{r},\vec{k},\omega)+\int d^3r'd^3r''G_0(\vec{r},\vec{r}\,',\omega)$$
$$\times\Sigma(\vec{r}\,',\vec{r}\,'',\omega)G(\vec{r}\,'',\vec{k},\omega)\;, \tag{2.5}$$

where G_0 is the zeroth-order Green's function. Taking the kinetic energy K as the zeroth-order Hamiltonian, one obtains with Eqs. (2.4) and (2.5) the Lippmann-Schwinger (LS) equation for the optical-model wave function[28–30,35,38]

$$\phi^{(+)}_{\vec{k}}(\vec{r})=\chi_{\vec{k}}(\vec{r})+\int d^3r'\,d^3r''\,G^{(+)}_0(\vec{r},\vec{r}\,',\epsilon_k)$$
$$\times\Sigma(\vec{r}\,',\vec{r}\,'',\epsilon_k+i\gamma)\phi^{(+)}_{\vec{k}}(\vec{r}\,'')\;, \tag{2.6}$$

where $\chi_{\vec{k}}(\vec{r})$ is a plane wave, $G^{(+)}_0$ the free-particle Green's function with outgoing-wave boundary condition, and Σ is the irreducible self-energy part[36]

$$\Sigma(\omega)=\Sigma(\infty)+M^{\mathrm{I}}(\omega)+M^{\mathrm{II}}(\omega)\;. \tag{2.7}$$

$\Sigma(\infty)$ is called the static part of the self-energy and includes the electron-nucleus interaction potential. The dynamic parts $M^{\mathrm{I,II}}(\omega)$ have the spectral representation[36] (in an arbitrary complete orthonormal single-particle basis)

$$M^{\mathrm{I,II}}_{pq}(\omega)=\sum_n\frac{m_p^{(n)}m_q^{(n)*}}{\omega-\omega^{(n)}\pm i\eta}\;. \tag{2.8}$$

The summation over n includes integration over the continuous part of the spectrum.

The many-particle scattering problem has thus been reduced exactly to an effective single-particle scattering problem. It follows from (2.6) that $\Sigma(\omega)$ has to be identified with the optical potential[15] describing elastic scattering from a correlated many-particle system. It is energy dependent, nonlocal, and becomes complex for energies above the lowest excitation threshold of the target molecule, thus accounting for the flux which is lost into the inelastic channels. Below the excitation threshold the many-body nature of the target system is reflected by the energy dependence of the optical potential.

The advantages of the above formulation of the optical potential compared to the more traditional approach[15] lies in the exact treatment of the exchange problem[30] and in the balanced way, in which correlations in the target and in the scattering complex are taken into account. The self-energy $\Sigma(\omega)$ can be calculated via diagrammatic many-body perturbation theory.[36] The particular approximation scheme which has been applied in the present work is described in Sec. IV A.

III. PROJECTION OF 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.[39] The former are associated with the existence of a barrier of the effective potential Σ. The latter originate from poles of the self-energy $\Sigma(\omega)$.[37,40] While it is straightforward to isolate the core-excited resonances, when $\Sigma(\omega)$ is given,[37,40] 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.[41,42] Here we apply the formalism developed in Ref. 42 to the effective single-particle scattering problem (2.6).

Assume that the optical potential Σ is such that the scattering amplitude exhibits an isolated single-particle resonance. Assume that a normalized square-integrable single-particle wave function $\phi_d(\vec{r})$ (which may be energy dependent) is given, which approximately describes the resonance (in a sense specified below). We may then define projectors in the single-particle Hilbert space according to

$$Q = |\phi_d\rangle\langle\phi_d| , \quad P = 1 - Q \; . \tag{3.1}$$

The extension of the formalism to several discrete states is straightforward.[42] The P space is spanned by orthonormal single-particle continuum states $|\hat{\vec{k}}^{(\pm)}\rangle$, constrained to be orthogonal to $|\phi_d\rangle$:

$$\langle \hat{\vec{k}}^{(\pm)} | \hat{\vec{k}}'^{(\pm)} \rangle = \delta(\epsilon_k - \epsilon_{k'})\delta(\Omega_k - \Omega_{k'}) \; , \tag{3.2a}$$

$$\langle \phi_d | \hat{\vec{k}}^{(\pm)} \rangle = 0 \; . \tag{3.2b}$$

Here and in the following the caret indicates orthogonality to the discrete state $|\phi_d\rangle$. The $|\hat{\vec{k}}^{(\pm)}\rangle$ can be obtained in closed form by orthogonalizing the free continuum to $|\phi_d\rangle$, giving[43–45]

$$|\hat{\vec{k}}^{(\pm)}\rangle = |\vec{k}\rangle - \frac{G_0^{(\pm)}|\phi_d\rangle\langle\phi_d|\vec{k}\rangle}{\langle\phi_d|G_0^{(\pm)}|\phi_d\rangle} \; , \tag{3.3}$$

where

$$G_0^{(\pm)} = (\epsilon_k - K \pm i\eta)^{-1} \tag{3.4}$$

is the free-particle Green's operator.

Applying now the well-known Feshbach projection-operator techniques,[15] one obtains[42]

$$T(\vec{k}',\vec{k}) = T_0(\vec{k}',\vec{k}) + T_{\text{dir}}^{(F)}(\vec{k}',\vec{k}) + T_{\text{res}}^{(F)}(\vec{k}',\vec{k}) \; , \tag{3.5}$$

where (the superscript F stands for Feshbach)

$$T_0(\vec{k}',\vec{k}) = \langle \vec{k}' | (K_{pp} - K) | \hat{\vec{k}}^{(+)} \rangle \; , \tag{3.6}$$

$$T_{\text{dir}}^{(F)}(\vec{k}',\vec{k}) = \langle \hat{\vec{k}}'^{(-)} | \Sigma_{pp} | \hat{\phi}_{\vec{k}}^{(+)} \rangle \; , \tag{3.7}$$

$$\begin{aligned} T_{\text{res}}^{(F)}(\vec{k}',\vec{k}) = {} & \langle \hat{\phi}_{\vec{k}'}^{(-)} | H_{PQ} | \phi_d \rangle [\epsilon_k - \epsilon_d - F(k)]^{-1} \\ & \times \langle \phi_d | H_{QP} | \hat{\phi}_{\vec{k}}^{(+)} \rangle \; , \end{aligned} \tag{3.8}$$

with the abbreviations

$$\begin{aligned} & H = K + \Sigma \; , \\ & \epsilon_d = \langle \phi_d | H | \phi_d \rangle \; , \end{aligned} \tag{3.9}$$

$$F(k) = \langle \phi_d | H_{QP} \hat{G}_{bg}^{(+)} H_{PQ} | \phi_d \rangle \; , \tag{3.10}$$

and $K_{pp} = PKP$, etc. The $|\hat{\phi}_{\vec{k}}^{(+)}\rangle$ are the background optical-model states defined as the solutions of the effective single-particle LS equation

$$|\hat{\phi}_{\vec{k}}^{(+)}\rangle = |\hat{\vec{k}}^{(+)}\rangle + \hat{G}_0^{(+)} \Sigma_{pp} |\hat{\phi}_{\vec{k}}^{(+)}\rangle \; , \tag{3.11}$$

with[43–45,42]

$$\begin{aligned} \hat{G}_0^{(+)} & = P(\epsilon_k - K_{pp} + i\eta)^{-1} P \\ & = G_0^{(+)} - \frac{G_0^{(+)}|\phi_d\rangle\langle\phi_d|G_0^{(+)}}{\langle\phi_d|G_0^{(+)}|\phi_d\rangle} \; . \end{aligned} \tag{3.12}$$

Finally, the resolvent operator $\hat{G}_{bg}^{(+)}$ in Eq. (3.10) is defined as

$$\hat{G}_{bg}^{(+)} = P(\epsilon_k - H_{pp} + i\eta)^{-1} P \; . \tag{3.13}$$

Note that the orthogonality constraint (3.2b) leads to the additional term T_0 in Eq. (3.5), which may be called the orthogonality scattering T matrix.[43–45] Its appearance is a consequence of the fact that the projectors P and Q defined in Eq. (3.1) do not commute with the kinetic energy operator K in contrast to the Feshbach formalism in its original form, where the projection is defined with respect to channels.[15] It is convenient to combine the orthogonality and the direct scattering T matrices to give the background scattering T matrix

$$T_{bg}(\vec{k}',\vec{k}) = T_0(\vec{k}',\vec{k}) + T_{\text{dir}}^{(F)}(\vec{k}',\vec{k}) \; . \tag{3.14}$$

A central quantity in the Feshbach formalism is the complex level-shift function $F(k)$ defined in Eq. (3.10). It defines the width function $\Gamma(\epsilon_k)$ and the real level-shift function $\Delta(\epsilon_k)$ via

$$\Delta(\epsilon_k)=\mathrm{Re}F(k)\ , \tag{3.15a}$$

$$\Gamma(\epsilon_k)=-2\,\mathrm{Im}F(k) \tag{3.15b}$$

for real positive k. It is seen from Eq. (3.8) that $F(k)$ shifts the real eigenvalue ϵ_d of H_{QQ} into the complex (energy or momentum) plane yielding the complex resonance pole of the T matrix.

To obtain a more explicit representation of the width and level-shift functions, we introduce the off-shell generalization of Eq. (3.11)

$$|\hat{\phi}^{(+)}_{\vec{k}'}(\epsilon_k)\rangle=|\hat{\vec{k}}'^{(+)}\rangle+\hat{G}_0^{(+)}(\epsilon_{k'})\Sigma_{pp}(\epsilon_k)\,|\hat{\phi}^{(+)}_{\vec{k}'}(\epsilon_k)\rangle\ . \tag{3.16}$$

When ϵ_k is below the first electronic excitation threshold of the target molecule, $\Sigma_{pp}(\epsilon_k)$ is Hermitian. Therefore the solutions of Eq. (3.16) for a fixed ϵ_k define a complete orthonormal set of single-particle states in P space and a spectral resolution of $\hat{G}^{(+)}_{bg}$. Defining the off-shell matrix element

$$V_{\vec{k}'}(\epsilon_k)=\langle\phi_d(\epsilon_k)\,|\,H_{QP}(\epsilon_k)\,|\,\hat{\phi}^{(+)}_{\vec{k}'}(\epsilon_k)\rangle \tag{3.17}$$

and using Eqs. (3.10) and (3.16), we have for energies ϵ_k below the excitation threshold

$$\Gamma(\epsilon_k)=2\pi\int d\Omega_k\,|\,V_{\vec{k}}(\epsilon_k)\,|^2\ , \tag{3.18}$$

$$\Delta(\epsilon_k)=\mathrm{P}\int d\Omega_{k'}dk'\,k'\frac{V_{\vec{k}'}(\epsilon_k)V^*_{\vec{k}'}(\epsilon_k)}{\epsilon_k-\epsilon_{k'}}\ , \tag{3.19}$$

where P denotes the principal-value integral. It is seen that $\Gamma(\epsilon_k)$ involves only the on-shell matrix element $V_{\vec{k}}(\epsilon_k)$, while off-shell matrix elements $V_{\vec{k}'}(\epsilon_k)$ are required to evaluate $\Delta(\epsilon_k)$ via Eq. (3.19). As a consequence, $\Delta(\epsilon_k)$ cannot be expressed as the Hilbert transform of $\Gamma(\epsilon_k)$, as is the case in ordinary potential scattering[41,42] as well as in the Feshbach formalism based on many-particle projection operators.[15,23]

The calculation of $T^{(F)}_{\mathrm{dir}}$ and $T^{(F)}_{\mathrm{res}}$ requires the solution of the background scattering LS equation (3.11) and the construction of the resolvent operator (3.13). In the present work this is achieved via a separable expansion of Σ_{pp}, which reduces the problem to the solution of a set of linear algebraic equations.[46] This expansion is equivalent to the use of the Schwinger variation principle for the T matrix.[46–48] More details are given in Sec. IV B.

The essence of the method is thus to solve the projected LS equation (3.11) instead of the original LS equation (2.6). Once the background optical-model states $|\hat{\phi}^{(+)}_{\vec{k}}\rangle$ and the corresponding propagator $\hat{G}^{(+)}_{bg}$ are given, the background scattering T matrix, the complex level shift, and the resonant T matrix are easily calculated. The formalism yields an exact decomposition of the T matrix into a resonant and a background term, which depends only on the choice of the discrete state $|\phi_d\rangle$.

In actual calculations it is more convenient to deal with real quantities, i.e., K-matrix elements or eigenphases. Therefore we show that Eq. (3.5) defines also a decomposition of the eigenphase sum into a resonant and a background term. Let us introduce the usual partial-wave representation (assuming a linear molecule for simplicity)

$$T(\vec{k}',\vec{k})=k^{-1}\sum_{l,l',m}T(k;l',l,m)Y_{l'm}(\Omega_{k'})Y^*_{lm}(\Omega_k)\ . \tag{3.20}$$

Defining a new resonant T matrix via

$$T_{\mathrm{res}}(\vec{k}',\vec{k})=\langle\hat{\phi}^{(+)}_{\vec{k}'}\,|\,H_{PQ}\,|\,\phi_d\rangle[\epsilon_k-\epsilon_d-F(k)]^{-1}\rangle\\ \times\langle\phi_d\,|\,H_{QP}\,|\,\hat{\phi}^{(+)}_{\vec{k}}\rangle\ , \tag{3.21}$$

we have the following relation between $T^{(F)}_{\mathrm{res}}$ of Eq. (3.8) and T_{res} of Eq. (3.21):

$$T^{(F)}_{\mathrm{res}}(k;l',l,m)=\sum_{l''}S_{bg}(k;l',l'',m)T_{\mathrm{res}}(k;l'',l,m)\ , \tag{3.22}$$

or in a matrix notation,

$$\underline{T}^{(F)}_{\mathrm{res}}=\underline{S}_{bg}\underline{T}_{\mathrm{res}}\ , \tag{3.23}$$

where

$$\underline{S}_{bg}=\underline{\mathbb{1}}-2\pi i\underline{T}_{bg}$$

and $\underline{T}_{bg}$ is defined in Eqs. (3.14) and (3.20). Defining now the resonant S matrix via

$$\underline{S}_{\mathrm{res}}=\underline{\mathbb{1}}-2\pi i\underline{T}_{\mathrm{res}}\ , \tag{3.24}$$

it follows that

$$\underline{S}=\underline{\mathbb{1}}-2\pi i\underline{T}=\underline{S}_{bg}\underline{S}_{\mathrm{res}}\ . \tag{3.25}$$

We have thus a factorization of the full S matrix into a resonant and a background term. Introducing the eigenphase sum

$$\delta^{\mathrm{sum}}=(2i)^{-1}\ln\det\underline{S}\ , \tag{3.26}$$

we have

$$\delta^{\mathrm{sum}}=\delta^{\mathrm{sum}}_{bg}+\delta^{\mathrm{sum}}_{\mathrm{res}}\ . \tag{3.27}$$

This is the desired decomposition of the eigenphase sum, which has been derived previously for an isolated Breit-Wigner resonance.[49]

For the present case of a single discrete state, T_{res} and $\delta^{\mathrm{sum}}_{\mathrm{res}}$ take a particularly simple form. From Eq. (3.21) we have

$$T_{\mathrm{res}}(k;l',l,m)=V_{kl'm}[\epsilon_k-\epsilon_d-F(k)]^{-1}V^*_{klm}\ , \tag{3.28}$$

with

$$V^*_{klm}=\langle\phi_d\,|\,H_{QP}\,|\,\hat{\phi}^{(+)}_{klm}\rangle\ . \tag{3.29}$$

Calculating $\delta^{\mathrm{sum}}_{\mathrm{res}}$ using Eqs. (3.24) and (3.26) leads to[41,49]

$$\delta^{\mathrm{sum}}_{\mathrm{res}}=-\tan^{-1}\frac{\Gamma(\epsilon_k)/2}{\epsilon_k-\epsilon_d-\Delta(\epsilon_k)} \tag{3.30}$$

which is the Breit-Wigner resonance formula with energy-dependent width and level shift.

A question which deserves some discussion is the appropriate choice of the discrete state $|\phi_d\rangle$. The formalism, as such, is applicable to any choice of the projector

Q. The problem is to ensure that a chosen discrete state "removes" a particular resonance, i.e., makes the background eigenphase sum δ_{bg}^{sum} a smooth function of energy in the vicinity of the resonance and transfers the resonance into the resonant eigenphase sum $\delta_{\text{res}}^{\text{sum}}$. In particular, the projection should not introduce spurious resonances into δ_{bg}^{sum} at energies where the full eigenphase sum is nonresonant.

There is a significant amount of literature devoted to the question of how to approximate shape resonances by L^2 wave functions and how to determine these wave functions variationally. The most common method in practical applications is the so-called stabilization method.[31,32,39] Here the Rayleigh-Ritz minimization of the energy is replaced by the concept of stabilization of the energy. In practice it is required that an eigenvalue, obtained by diagonalizing H in an L^2 basis, should be stable with respect to the extension of the basis set or with respect to a scaling of the basis functions. Stable eigenvalues are believed to approximate resonances. Another approach is to minimize the variance of the Hamiltonian, $\langle H^2 \rangle - \langle H \rangle^2$, employing L^2 test functions.[50–52] It should be stressed that one needs usually only a crude estimate of the discrete state when applying the Feshbach formalism, since the real level shift $\Delta(\epsilon_k)$ corrects for the error, yielding the exact resonance energy.

IV. APPROXIMATIONS AND COMPUTATIONAL METHODS

A. Approximation scheme for the optical potential

In many-body perturbation theory, Σ is defined via a diagrammatic perturbation expansion.[36] To construct approximations for Σ, one may proceed either order by order or by performing suitable infinite partial summations of diagrams. The first step is to define a complete manifold of single-particle states. These are most conveniently chosen as the Hartree-Fock (HF) single-particle states. In this representation, the optical potential may be written as [recalling Eqs. (2.7) and (2.8)]

$$\begin{aligned}\Sigma(\omega) = \Sigma_{SE} + \Sigma_{\text{pol}}(\omega) = \Sigma_{SE} + [\Sigma(\infty) - \Sigma_{SE}] \\ + M^{\text{I}}(\omega) + M^{\text{II}}(\omega) \,,\end{aligned} \tag{4.1a}$$

where

$$\Sigma_{SE} = v_{en} + \sum_i (J_i - K_i) \tag{4.1b}$$

is the well-known static-exchange potential, v_{en} is the interaction of the projectile with the nuclei, and J_i and K_i are the usual Coulomb and exchange operators. Σ_{pol} is given by all linked proper diagrams representing the many-body perturbation series in terms of the residual interaction[28,36] (the full interaction Hamiltonian minus the HF Hamiltonian).

The simplest approximation for Σ is the static-exchange approximation $\Sigma = \Sigma_{SE}$. In this approximation the motion of the projectile electron is governed by the average interaction potential with all particles of the target, while the dynamic distortion of the molecular charge distribution due to the presence of the incident electron as well as target correlation are neglected. When representing Σ in the HF single-particle manifold, terms of first order in the residual interaction cancel each other exactly, so that the net first-order contribution is zero.[36]

The dynamic distortion of the target (polarization) and the correlation in the target state are described by $M^{\text{I,II}}$ of Eq. (4.1). Contributions from these terms appear first in second order. The second-order optical potential has been used for electron-atom[53–55] and electron-molecule[56] scattering with considerable success. However, it has recently been shown[57] that one has to go beyond the second-order optical potential to obtain accurate results for shape resonances.

The second-order optical potential has the correct analytic structure as defined in Eqs. (2.7) and (2.8). This structure is not maintained when one straightforwardly expands Σ beyond second order.[58] A well-defined and rather simple approximation scheme for $M^{\text{I,II}}$, which is based on the infinite partial summation of certain classes of important diagrams such that the correct analytic structure is restored, is the 2ph-TDA (two-particle-hole Tamm-Dancoff approximation).[58] The energy-independent term $\Sigma(\infty) - \Sigma_{SE}$, whose perturbation expansion starts in third order, is neglected in the 2ph-TDA. The 2ph-TDA scheme can be derived in various ways, as described in detail in Ref. 58. The 2ph-TDA self-energy has been extensively used in the calculation of ionization potentials of molecules.[59] Recently it has also been applied to electron-molecule scattering with very promising results.[57]

In the 2ph-TDA one obtains separately the terms $M^{\text{I}}(\omega)$ and $M^{\text{II}}(\omega)$ of Eq. (2.8). These are obtained by solving directly for the eigenvalues $\omega^{(n)}$ and Dyson amplitudes $m_p^{(n)}$ of Eq. (2.8) via an eigenvalue problem which formally reads

$$(\omega^{(n)} + \epsilon_j - \epsilon_k - \epsilon_l)\mathcal{X}_{jkl}^{(n)} - \sum_{j',k'<l'} C_{jkl,j'k'l'} \mathcal{X}_{j'k'l'}^{(n)} = 0 \,, \tag{4.2}$$

where the ϵ_i denotes the HF single-particle energies. The Dyson amplitudes $m_p^{(n)}$ follow from the eigenvector components of Eq. (4.2) according to

$$m_p^{(n)} = \sum_{\substack{k<l \\ j}} v_{pj[kl]} \mathcal{X}_{jkl}^{(n)} \,. \tag{4.3}$$

The index space for M^{I} is restricted to particle-particle-hole, while the index space for M^{II} is confined to hole-hole-particle, i.e.,

$$\begin{aligned} &j = \text{hole;} \quad k,l = \text{particle} \quad \text{for } M^{\text{I}} \,, \\ &k,l = \text{hole;} \quad j = \text{particle} \quad \text{for } M^{\text{II}} \,. \end{aligned} \tag{4.4}$$

The matrix C is given by

$$\begin{aligned} C_{jkl,j',k',l'}^{\text{I,II}} = \pm(&-v_{kl[k',l']}\delta_{jj'} + v_{j'l[jl']}\delta_{kk'} + v_{j'k[jk']}\delta_{ll'} \\ &- v_{j'l[jk']}\delta_{kl'} - v_{j'k[jl']}\delta_{lk'}) \,, \end{aligned} \tag{4.5}$$

where the $(-)$ sign is for M^{I} and the $(+)$ sign for M^{II}. In Eqs. (4.3)–(4.5) $v_{ij[kl]} = v_{ijkl} - v_{ijlk}$ denotes the antisymmetrized Coulomb matrix element.

In the 2ph-TDA defined above, the term M^{I} accounts for the relaxation of the target electrons and the associated change in the pair correlation energies in the target state. The term M^{II} accounts for the increase of the pair correlation energies due to the (temporary) attachment of an additional electron. Neglecting M^{II} is equivalent to neglecting target-state correlation and performing a configuration interaction (CI) calculation on the temporary ion including all two-particle—one-hole excitations, i.e., "2p-1h-TDA".[58] The inclusion of both M^{I} and M^{II} guarantees a balanced treatment of target correlation and polarization.[58]

B. Approximation scheme used in solving the one-body Lippmann-Schwinger equation

It is well known that molecular continuum wave functions are difficult to obtain. This is a consequence of the nonspherical nature of the effective electron-molecule interaction potential. To overcome this difficulty, L^2 methods were developed. The most successful of these methods are the R-matrix[60–62] and T-matrix[63] expansion methods. The latter has been improved by adopting the Schwinger variational expression for the T matrix.[46–48,64–66] A related method in which one solves linear algebraic equations has been proposed recently by Schneider and Collins.[67]

In the present work we use the Schwinger variational principle to treat the background scattering problem. This is equivalent to representing the optical potential Σ in the separable form

$$\Sigma^{(S)}=\sum_{\alpha,\alpha'}\Sigma\,|\,\alpha\rangle\lambda_{\alpha\alpha'}\langle\alpha'\,|\,\Sigma\ , \tag{4.6}$$

with $(\lambda^{-1})_{\alpha\alpha'}=\langle\alpha'\,|\,\Sigma\,|\,\alpha\rangle$. In (4.6) the functions $\langle\vec{r}\,|\,\alpha\rangle$, $\vec{r}$ being the coordinate of the scattered electron, are square-integrable energy-independent basis functions. With the separable potential $\Sigma^{(S)}$, the direct scattering potential Σ_{pp} in Eq. (3.7) is also separable. The expression for the corresponding $T_{\mathrm{dir}}^{(F)}$ of Eq. (3.7) reads then

$$T_{\mathrm{dir}}^{(F)}(\vec{\mathrm{k}}\,',\vec{\mathrm{k}}\,)=\sum_{\alpha,\alpha'}\langle\vec{\mathrm{k}}\,'\,|\,\widetilde{X}\,|\,\alpha\rangle B_{\alpha\alpha'}\langle\alpha'\,|\,X\,|\,\vec{\mathrm{k}}\rangle\ , \tag{4.7}$$

where

$$X=\Sigma-\Sigma G_0^{(+)}\,|\,\phi_d\rangle\frac{1}{\langle\phi_d\,|\,G_0^{(+)}\,|\,\phi_d\rangle}\langle\phi_d\,| \tag{4.8}$$

and

$$(\underline{B}^{-1})_{\alpha\alpha'}=\langle\alpha'\,|\,(\Sigma-XG_0^{(+)}\Sigma)\,|\,\alpha\rangle\ . \tag{4.9}$$

Here $\widetilde{X}$ denotes the transpose of X.

$T_{\mathrm{dir}}^{(F)}$ has thus been expressed in terms of the free-particle Green's function $G_0^{(+)}$ and plane-wave state $|\,\vec{\mathrm{k}}\rangle$, while the orthogonalized $\hat{G}_0^{(+)}$ and $|\,\hat{\vec{\mathrm{k}}}^{(+)}\rangle$ appearing in Eq. (3.7) have been eliminated. To achieve the same for the background optical-model states, Green's function, and T matrix, we rewrite Eq. (3.11) and (3.13) as

$$|\,\hat{\phi}_{\vec{\mathrm{k}}}^{(+)}\rangle=|\,\vec{\mathrm{k}}\rangle+G_0^{(+)}T_{bg}\,|\,\vec{\mathrm{k}}\rangle\ , \tag{4.10a}$$

$$\hat{G}_{bg}^{(+)}=G_0^{(+)}+G_0^{(+)}T_{bg}G_0^{(+)}\ , \tag{4.10b}$$

where the operator T_{bg} is defined via

$$\langle\vec{\mathrm{k}}\,'\,|\,T_{bg}\,|\,\vec{\mathrm{k}}\rangle=T_{bg}(\vec{\mathrm{k}}\,',\vec{\mathrm{k}}\,)=T_0(\vec{\mathrm{k}}\,',\vec{\mathrm{k}}\,)+T_{\mathrm{dir}}^{(F)}(\vec{\mathrm{k}}\,',\vec{\mathrm{k}}\,)\ . \tag{4.10c}$$

Using (4.7), $|\,\hat{\phi}_{\vec{\mathrm{k}}}^{(+)}\rangle$, $\hat{G}_{bg}^{(+)}$, and $T_{bg}(\vec{\mathrm{k}}\,',\vec{\mathrm{k}}\,)$ are all expressed in terms of $G_0^{(+)}$ and $|\,\vec{\mathrm{k}}\rangle$.

Once the background scattering problem is solved, one may evaluate the quantities $V_{\vec{\mathrm{k}}}$, Γ, and Δ of Eqs. (3.15)–(3.19). Using the operator identity $(\epsilon_k-K)G_0^{(+)}=1$, the kinetic-energy operator K may be removed from all products of the form KG_0,G_0K, leading to the working equations for the on-shell matrix element

$$V_{\vec{\mathrm{k}}}(\epsilon_k)=\langle\phi_d\,|\,[\epsilon_k+\Sigma+(\epsilon_kG_0^{(+)}-1+\Sigma G_0^{(+)})T_{bg}]\,|\,\vec{\mathrm{k}}\rangle \tag{4.11}$$

and the complex level-shift function

$$\begin{aligned}\langle\phi_d\,|\,H_{QP}\hat{G}_{bg}^{(+)}H_{PQ}\,|\,\phi_d\rangle\\ =\langle\phi_d\,|\,(&T_{bg}-K-2\Sigma-\epsilon_k+\epsilon_k^2G_0^{(+)}+\epsilon_k^2G_0^{(+)}T_{bg}G_0^{(+)}-\epsilon_kG_0^{(+)}T_{bg}-\epsilon_kT_{bg}G_0^{(+)}+\epsilon_kG_0^{(+)}\Sigma+\epsilon_k\Sigma G_0^{(+)}\\ &+\epsilon_kG_0^{(+)}T_{bg}G_0^{(+)}\Sigma+\epsilon_k\Sigma G_0^{(+)}T_{bg}G_0^{(+)}-T_{bg}G_0^{(+)}\Sigma-\Sigma G_0^{(+)}T_{bg}+\Sigma G_0^{(+)}\Sigma+\Sigma G_0^{(+)}T_{bg}G_0^{(+)}\Sigma)\,|\,\phi_d\rangle\ .\end{aligned} \tag{4.12}$$

In Sec. V, Γ and Δ are evaluated directly from Eq. (3.15) with the complex level shift of (4.12). The eigenphase sums $\delta_{bg}^{\mathrm{sum}}$ and $\delta_{\mathrm{res}}^{\mathrm{sum}}$ are obtained as described in Sec. III [Eqs. (3.20)—(3.30)].

It should be mentioned that similar projection techniques[68] have been used by Lucchese *et al.*[69] to eliminate spurious resonances in static-exchange calculations of photoionization cross sections. In these calculations the orthogonality scattering problem is approximately solved using a separable expansion of $K_{pp}-K+\Sigma_{pp}$. In the present work, the orthogonality scattering "potential" $K_{pp}-K$ is treated exactly and only the potential Σ_{pp} is approximated by a separable expansion. This is important in view of the fact that the kinetic-energy operator is an unbounded operator.

C. Technical details of the calculation

The Hartree-Fock calculation to define the single-particle manifold is performed employing the $(11s,7p)$

TABLE I. Gaussian basis sets for e-N_2 scattering. Types of exponents (on the atoms) are listed. Contraction coefficients are given in parentheses, basis functions are separated by semicolons (";"), and primitives by commas (",").

	Hartree-Fock set
s	13 515.3(0.001 43), 1998.96(0.011 61), 439.998(0.062 74), 120.8999(0.253 27), 38.4711(0.750 77); 13.4578;4.992 99(0.887 31), 1.659 81(0.135 92); 0.736 372(0.484 16), 0.293 648(0.553 18); 0.123 902
p_x,p_y,p_z	35.9111(0.017 27), 8.480 42(0.104 26), 2.705 63(0.345 58), 1.001 99(0.659 66); 0.400 617; 0.168 433; 0.076 081
$d_{xx\text{-}yy}$,d_{zz} d_{xy},d_{xz},d_{yz}	1.5; 0.5
	Discrete-state set
p_x	The uncontracted p_x basis of the HF set minus the last function with exponent 0.076 081
d_{xz}	The d_{xz} basis of the HF set
	Schwinger set [$\langle \vec{r} \mid \alpha \rangle$ of Eq. (4.5)–(4.8)]
p_x	The uncontracted p_x basis of the HF set
d_{xz}	The d_{xz} basis of the HF set
	Quadrature set (see last paragraph of Sec. IV C)
p_x	The p_x basis of the Schwinger set plus 300.0; 100.0; 30.0; 0.02; 0.006; 0.002
d_{xz}	The d_{xz} basis of the Schwinger set plus 300.0; 100.0; 30.0; 0.02; 0.006; 0.002

Gaussian basis set of Salez and Veillard[70] contracted to $(5s,4p)$ and augmented by two d functions to allow for more flexibility in describing polarization. Table I gives the basis set of this calculation.

In constructing the optical potential, the static-exchange potential is calculated using Eq. (4.1b). The 2ph-TDA contribution is built up in two steps. In the first step two-electron integrals involving the basis functions are transformed to integrals over molecular orbitals [$v_{pj[kl]}$ of Eq. (4.5)]. In the second step the Dyson amplitudes are calculated by solving the eigenvalue problem, Eqs. (4.2—4.5). It is then a simple step to construct $M_{pq}^{\mathrm{I,II}}(\omega)$ by Eq. (2.8) for each energy ω.

The stabilization technique[31,32,39] is used to construct the discrete state $| \phi_d \rangle$. The energy-dependent single-particle Hamiltonian $H(\epsilon_k)=K+\Sigma(\epsilon_k)$ is diagonalized in basis sets of various sizes and a stable eigenvalue (stable with respect to changes of the basis) is searched. We have found that it was sufficient to omit the most diffuse functions from the above-mentioned HF basis in order to obtain an estimate for the stabilized $| \phi_d \rangle$. The basis set used to define the discrete state is also given in Table I. Note that only a crude estimate is needed for $| \phi_d \rangle$, as the level shift $\Delta(\epsilon_k)$ will shift the resonance energy to the correct position. Note also that $| \phi_d \rangle$ and ϵ_d depend on ϵ_k.

Various basis sets were tried for the functions $\{ \langle \vec{r} \mid \alpha \rangle \}$ of Eq. (4.6), which define the separable expansion of Σ, in order to check the stability of the expression (4.7) for the direct T matrix with respect to changes of the basis set. In the results reported here this set is taken to be identical with the above uncontracted $(11s,7p,2d)$ set (see Table I). We have found that the results are insensitive to extensions of this basis.

The last technical point to be discussed is the calculation of the integrals such as $\langle \alpha \mid \Sigma \mid \vec{k} \rangle$ and $\langle \alpha \mid \Sigma G_0^{(+)} \Sigma \mid \alpha' \rangle$ which are needed in the calculations of Eqs. (4.7)—(4.12). These are calculated by using a quadrature formula constructed from a set of Gaussian functions much larger than the set $\langle \vec{r} \mid \alpha \rangle$. This set (also shown in Table I) is inserted between Σ and $| \vec{k} \rangle$ or Σ and $G_0^{(+)}$. Convergence of such insertions has been tested for the terms like $\langle \alpha \mid \Sigma G_0^{(+)} \Sigma \mid \alpha' \rangle$ by McKoy and co-workers.[64,65] This choice of quadrature enables us to use standard codes for calculating all needed integrals of the theory, e.g., Coulomb matrix elements, or matrix elements of the free-particle Green's function $G_0^{(+)}$. Finally we mention that the basis sets of Table I are nonorthogonal. The overlap integrals of the basis functions are explicitly taken into account in the actual calculations.

In summary, the sequence of computational steps that have to be performed to get the final results is as follows: (i) Perform a standard Hartree-Fock calculation to define the single-particle manifold. (ii) Using this manifold, construct the static-exchange potential [Eq. (4.1b)] and the 2ph-TDA self-energy part via Eqs. (2.8) and (4.2)—(4.5). (iii) Perform a stabilization calculation to define the discrete state, i.e., diagonalize the single-particle Hamiltonian, Eq. (3.9), in a restricted subspace of the single-particle basis. (iv) Solve the background scattering problem using Eqs. (4.7) and (4.10) and calculate the background eigenphase sum. (v) Construct the coupling-matrix elements V_{klm} of Eqs. (3.29) and (4.11), the complex level shift of Eq. (4.12), and the resonant T matrix and eigenphase sum via Eqs. (3.28) and (3.30).

V. RESULTS

We have chosen the $^2\Pi_g$ shape resonance of the N_2 molecule to test the method described in the preceding sections. We confine ourselves to fixed-nuclei calculations at the equilibrium geometry $R_0 = 2.068$ a.u. Results are presented for the static-exchange approximation and for the 2ph-TDA. For both we show the explicit separation of the eigenphase sum into a resonant and a background term and the calculated width and level-shift functions. To our knowledge these are the first calculations which provide an explicit separation of the eigenphase sum into resonance and background contribution for a real molecule.

A. Static-exchange results

The separation of the $^2\Pi_g$ eigenphase sum into background (dashed-dotted) and resonance (dashed) contributions in the static-exchange approximation is shown in Fig. 1(a). The background eigenphase sum δ_{bg}^{sum} is obtained using the background T matrix of Eq. (4.10c) and the partial-wave representation defined in Eq. (3.20). The resonance eigenphase sum $\delta_{\text{res}}^{\text{sum}}$ is obtained from Eq. (3.30). We have checked numerically that δ_{bg}^{sum} and $\delta_{\text{res}}^{\text{sum}}$ add up to the full eigenphase sum δ^{sum} [full line in Fig. 1(a)] as it should according to Eq. (3.27). δ^{sum} can be calculated directly by using the potential (4.6) and solving the Lippmann-Schwinger equation (2.6), see Ref. 57.

Figure 1(a) shows that the background contribution in the $^2\Pi_g$ symmetry is relatively small and weakly energy dependent. The resonant contribution shows the typical resonance behavior, i.e., a rapid increase in the eigenphase sum near 3.8 eV. The location of the resonance is ~1.5 eV too high compared to the known experimental value.[71]

The corresponding width and level-shift functions are shown in Fig. 1(b). These are obtained from Eqs. (3.15) and (4.12). The level shift Δ of Fig. 1(b) is the Hilbert transform of the width Γ. This follows from Eqs. (3.16)–(3.19) and the fact that the effective single-particle Hamiltonian H is energy independent in the static-exchange approximation. In the static-exchange approximation our method is equivalent to that of Hazi.[24] If the same discrete state is chosen, the width and level-shift functions obtained by the two methods are identical.

B. Results in the 2ph-TDA

The full line in Fig. 2(a) shows the eigenphase sum obtained in the 2ph-TDA. The dashed-dotted and dashed lines show its separation into a background and resonant contribution, respectively. As before, we have checked that δ_{bg}^{sum} and $\delta_{\text{res}}^{\text{sum}}$ add up to the eigenphase sum δ^{sum} obtained directly using the potential of Eq. (4.6).[57]

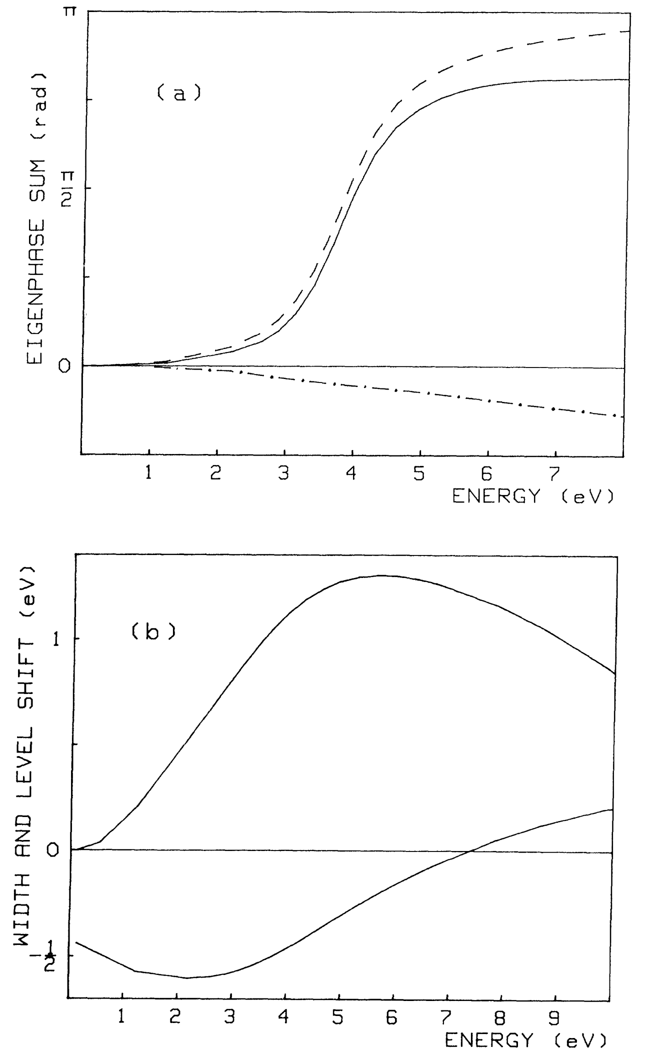

FIG. 1. (a) Eigenphase sum of the $^2\Pi_g$ resonance in e-N_2 scattering in the static-exchange approximation. Full line denotes the full eigenphase sum, the dashed line denotes resonant eigenphase sum, and the dashed-dotted line denotes the background contribution. (b) Width and level-shift functions in the static-exchange approximation as a function of energy.

It is notable that the background contribution is now considerably smaller than in the static-exchange approximation. The resonance eigenphase sum shows a rapid rise near 2.3 eV. This rise is shifted by 1.5 eV (and is much steeper) compared to the static-exchange result. The resonance position is now close to the experimental value of 2.35 eV.[71] This is a consequence of including correlation and polarization which are neglected in the static-exchange approximation.

The width and level-shift functions are shown in Fig. 2(b) (full lines). The width function obtained in the 2ph-TDA is smaller than the static-exchange result by about a factor of two at all energies. [Note the difference in scale when comparing Figs. 1(b) and 2(b)]. For comparison, the width and level-shift functions calculated by Hazi[25] are

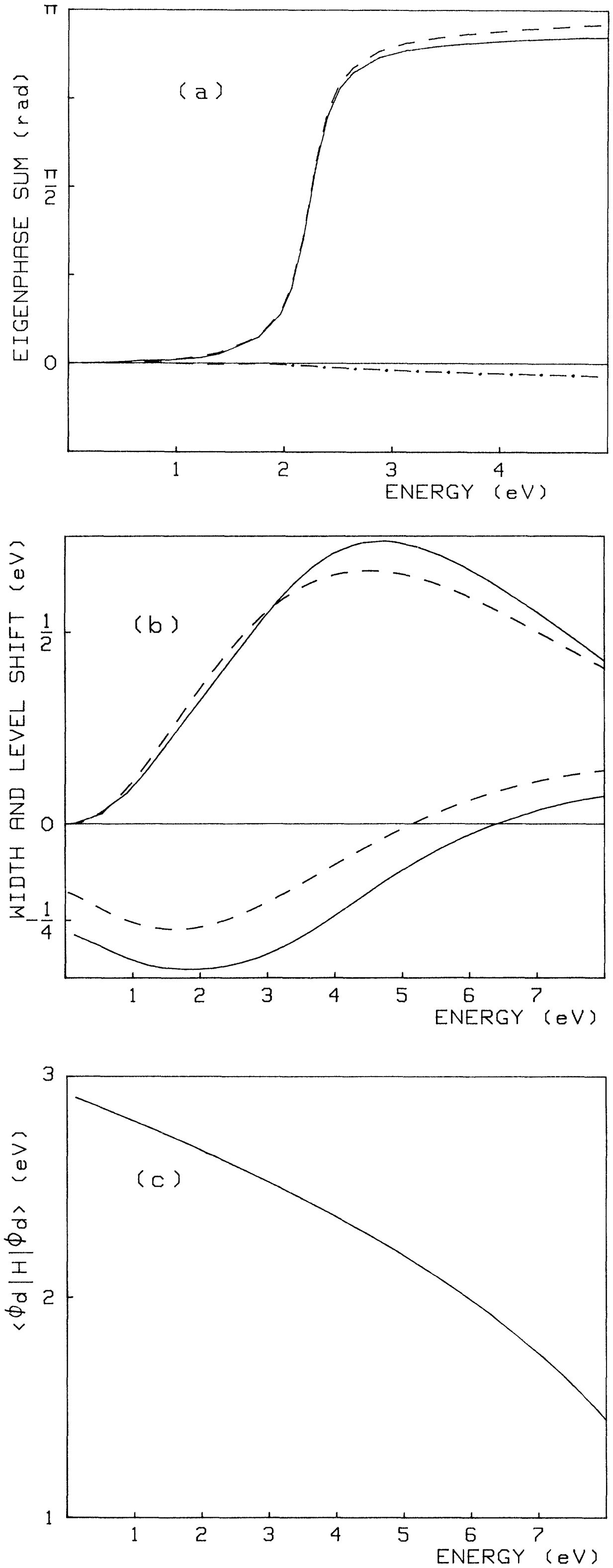

FIG. 2. (a) Eigenphase sum of the $^2\Pi_g$ resonance in e-N$_2$ scattering in the 2ph-TDA. The labeling of the curves is as in Fig. 1(a). (b) Width and level-shift functions in the 2ph-TDA as a function of energy. Full lines denote results of present work while the dashed lines stand for the results of Hazi (Ref. 25). (c) Discrete-state energy $\epsilon_d = \langle \phi_d \,|\, H(\epsilon_k) \,|\, \phi_d \rangle$ as a function of the energy ϵ_k.

included in Fig. 2(b) (dashed lines). The agreement between the two width functions (in particular near the resonance energy) is excellent, considering that the two calculations are performed with completely different methods and that different basis sets are used.

The eigenvalue $\epsilon_d = \langle \phi_d \,|\, H \,|\, \phi_d \rangle$ as a function of the energy ϵ_k is shown in Fig. 2(c). The energy dependence of ϵ_d is a consequence of the energy dependence of Σ. Because of this energy dependence of Σ, the level shift Δ of Fig. 2(b) is also no longer the Hilbert transform of Γ. This is in contrast to the width and level-shift function of Hazi[25] which are Hilbert transforms of each other. In Fig. 3 we compare $\delta_{\text{res}}^{\text{sum}}$ of the present work (full line) with the resonant eigenphase sum calculated from Γ and Δ given by Hazi[25] using Eq. (3.30) (stars). It is seen that the two results are in excellent agreement. In particular, the resonance positions agree to an accuracy of $\sim$0.1 eV. The widths at the resonant position are also in excellent agreement [see Fig. 2(b)].

Finally, we have collected in Table II some representative results on the angular distribution of the background and resonance scattering at three different energies, namely, very near the resonance energy (2.287 eV) and at the wings of the resonance (1.965 and 2.879 eV). The upper panel of the table gives the $^2\Pi_g$ background K matrix K_{bg} corresponding to the T matrix of Eqs. (3.14) and (4.10). It is seen that the main contribution to the $^2\Pi_g$ background scattering comes from a mixture of $d(l=2)$ and $f(l=4)$ waves. The resulting background $^2\Pi_g$ eigenphase sum is also given in the table.

The on-shell discrete-state-continuum coupling-matrix elements V_{klm} of Eq. (3.29) are shown next in Table II. It is seen that here the main contribution is a $d(l=2)$ wave, in accord with the well-known assignment of the angular dependence of this resonance.[72] Finally, the resonance parameters Γ, Δ, and ϵ_d [see Eqs. (3.9), (3.10), (3.15), and (4.12)] for these energies are given, as well as the resonant eigenphase sum calculated with Eq. (3.30). The results in

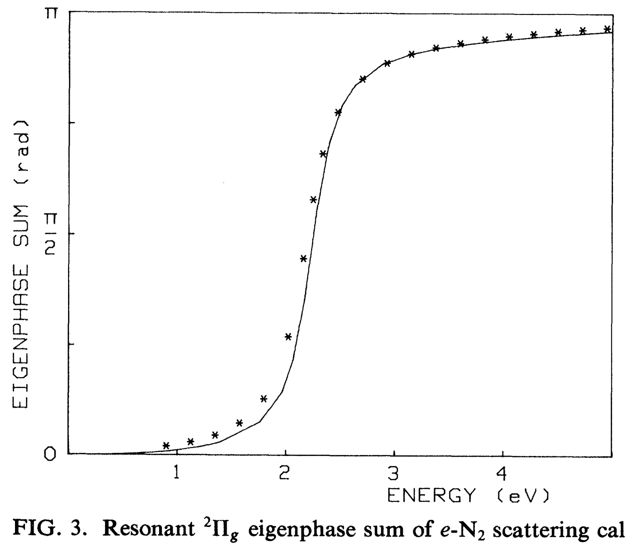

FIG. 3. Resonant $^2\Pi_g$ eigenphase sum of e-N$_2$ scattering calculated in this work (full line) compared to the results of Hazi (Ref. 25) (stars).

Table II represent the first *ab initio* analysis of the angular dependence of the background and resonance contribution for an electron-molecule scattering resonance.

VI. DISCUSSION AND CONCLUSIONS

We have presented a new method to separate the T matrix (or the eigenphase sum) for fixed-nuclei electron-molecule scattering into a smooth background term and a resonant term, which may vary rapidly with energy ϵ_k and internuclear distance R. The relevance of this separation lies in the treatment of nuclear motion in electron-molecule scattering. Owing to its weak dependence on ϵ_k and R, the background scattering T matrix can be treated in the adiabatic-nuclei approximation.[17,18,73] The resonant T matrix, on the other hand, can be calculated to a higher level of sophistication by treating properly the nuclear dynamics in the short-lived negative-ion state, which is governed by an energy-dependent, complex, and nonlocal potential.[3–14]

In the present method the many-body optical-potential formalism[28] is employed to reduce the fixed-nuclei electron-molecule scattering problem to an effective single-particle problem. The method is particularly well suited to describe shape resonances, which are due to the existence of a barrier in the effective electron-molecule interaction potential. The use of the many-body optical potential guarantees a balanced treatment of polarization effects in the negative ion and correlation effects in the target molecule. This is crucial to obtain accurate positions and widths of resonances.[57,74]

The Schwinger variational principle[46–48] is used to solve the single-particle scattering problem. The above-mentioned separation of the T matrix is obtained by solving a projected LS equation, implying orthogonality to a suitably chosen discrete state. The solutions are the background scattering states and are obtained explicitly. Once the background scattering problem is solved, the calculation of the width $\Gamma(\epsilon_k)$ and level shift $\Delta(\epsilon_k)$ is straightforward.

Pioneering calculations of $\Gamma(\epsilon_k)$ and $\Delta(\epsilon_k)$ have been performed by Hazi and co-workers for shape resonances and doubly excited autoionizing valence states.[4,23–26] In these calculations the solution of the electron-molecule scattering problem is avoided by using Stieltjes imaging[75] to construct a smooth function $\Gamma(\epsilon_k)$ from a discretized representation of the background scattering continuum. This approach yields only the total width $\Gamma(\epsilon_k)$, from which $\Delta(\epsilon_k)$ may be obtained by Hilbert transformation.[23–25] These data are sufficient to construct the angle-integrated resonant T matrix.[3–5] No information is obtained, however, on the background scattering T matrix and the angular dependence of the resonant scattering. Despite these limitations, the method has been very successful and has provided the basis for the *ab initio* treatment of vibrational excitation in N_2 (Refs. 3 and 5) and dissociative attachment in F_2 (Ref. 4). The knowledge of the background scattering T matrix may be important, however, for broader resonances,[76] for electron-polar molecule scattering, or the description of virtual-state effects.[77]

TABLE II. Background and resonance angular dependence of the $^2\Pi_g$ symmetry in e-N_2 scattering. (numbers in parentheses indicate powers of 10)

		$E=1.965$ eV				$E=2.287$ eV				$E=2.879$ eV		
	$l \backslash l'$	2	4	6	$l \backslash l'$	2	4	6	$l \backslash l'$	2	4	6
K_{bg}	2	−0.202(−1)			2	−0.383(−1)			2	−0.693(−1)		
	4	−0.132(−1)	0.800(−2)		4	−0.128(−1)	0.113(−1)		4	−0.524(−2)	0.134(−1)	
	6	−0.495(−4)	0.303(−4)	0.115(−6)	6	−0.555(−4)	0.498(−4)	0.219(−6)	6	0.273(−4)	0.739(−4)	0.409(−6)
δ_{bg}^{sum}			−0.0123				−0.0270				−0.0562	
	l	ReV_{klm}	ImV_{klm}		l	ReV_{klm}	ImV_{klm}		l	ReV_{klm}	ImV_{klm}	
V_{klm}	2	0.429(−1)	0.873(−3)		2	0.476(−1)	−0.183(−2)		2	0.551(−1)	0.383(−2)	
$m=1$ (a.u.)	4	0.364(−3)	0.563(−3)		4	0.781(−3)	−0.600(−3)		4	0.141(−2)	0.270(−3)	
	6	0.886(−6)	0.211(−5)		6	0.269(−5)	−0.200(−5)		6	0.643(−5)	−0.140(−5)	
Γ (eV)			0.314				0.388				0.523	
Δ (eV)			−0.378				−0.372				−0.346	
ϵ_d (eV)			2.667				2.623				2.537	
$\delta_{\text{res}}^{\text{sum}}$			0.450				1.757				2.778	

The limitations of Hazi's method are overcome in the present approach. We obtain explicitly the background T matrix or K matrix and the information on the angular distribution of the resonant scattering. Therefore, it is possible to verify the applicability of the adiabatic-nuclei approximation for the background scattering. As shown in the application to the 2.3-eV shape resonance in e-N_2 scattering, the background eigenphase sum is indeed small and a smooth function of energy. These results represent the first *ab initio* analysis of the background contribution in resonant electron-molecule scattering. Another more technical advantage of the present method is that the level shift $\Delta(\epsilon_k)$ is obtained directly rather than by taking the Hilbert transform of $\Gamma(\epsilon_k)$. It is therefore not necessary to compute $\Gamma(\epsilon_k)$ for all energies; all calculations can be confined to the energy interval of interest.

The present method differs from Hazi's approach[23-25] in that the projection of the resonance is performed in a single-particle Hilbert space rather than in the Hilbert space of electronic $(N+1)$-particle states. The discrete state in the present work is a single-particle state, while it is an $(N+1)$-particle determinant or configuration interaction wave function in Hazi's method. Because of this difference in the definition of the projection, the discrete-state energies, width functions, and level shifts obtained with the two methods are not identical, at least beyond the static-exchange level of approximation. The test calculation for the 2.3-eV shape resonance in N_2 has shown, however, that, nevertheless, very similar results are obtained in the two calculations. In particular, the resonance energies $E_{\text{res}} = \epsilon_d + \Delta(E_{\text{res}})$ and widths $\Gamma(\epsilon_{\text{res}})$ agree to better than 0.1 eV.

While the reduction of the $(N+1)$-electron problem to an effective single-particle problem in the optical potential formalism represents an enormous simplification and allows us to solve the scattering problem explicitly with proper boundary conditions, certain difficulties arise in the present approach from the explicit energy dependence of the optical potential Σ which results from the virtual excitation of the target electrons. As a consequence, the "potential energy curve" $V_1(R) = V_0(R) + \epsilon_d(\epsilon_k, R)$ of the discrete state is explicitly dependent on the energy ϵ_k of the scattered electron. Moreover, the energy dependence of Γ and Δ has two sources: the "usual" energy dependence which exists already in the static-exchange approximation and an additional energy dependence arising from the explicit dependence of Σ on ϵ_k. The energy dependence of Σ may complicate the treatment of the nuclear dynamics within the Feshbach projection-operator approach. Calculations of nuclear dynamics using the present method are in progress.

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