Complex coordinate rotation of the electron propagator

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It is now widely appreciated that the real poles of the electron propagator $G(E)$ yield information on the ionization potentials and electron affinities of the stationary states of an atom or molecule. It is herein shown that application of the Aguilar–Balslev–Combes–Simon coordinate transformation, $r \rightarrow r \exp(i\Theta)$, to $G(E)$ yields an analytically continued complex propagator $G(Z, \Theta)$ whose complex poles correspond to the complex electron affinities associated with nonstationary, resonance states of an atomic or molecular anion. As an initial application of the coordinate rotation technique we derive and discuss the working equations for a coordinate rotated propagator which is correct to second order in the electron–electron interaction. This is followed by use of the formalism in a model study of a ^2P shape resonance in the Be atom. Our second-order results for this system are then compared to those obtained by previous authors employing static exchange, and static-exchange plus cutoff polarization methods.

I. INTRODUCTION

Electron–atom and electron–molecule shape resonances can be thought of as metastable anionic states which decay by electron emission. The possibility of shape resonance formation occurs when the effective potential governing the interaction of an incident electron and the target atom or molecule exhibits long-range repulsion and short-range attraction; this gives rise to a penetrable (usually centrifugal) barrier within which the incident electron may be temporarily bound. Relative to their neutral parents, shape resonances have a well-defined positive energy E and lifetime $\tau(\tau \equiv \hbar/\Gamma$, where Γ is the resonance width) which typically lie on the respective intervals (0–10) eV and $(10^{-15}-10^{-13})$ sec. Much of the experimental work on shape resonances was reviewed by Schulz,[1] who pioneered the use of electron transmission spectroscopy for studying these metastable states.

Much of the difficulty encountered in previous theoretical treatments of shape resonances based either on the use of the scattering matrix[2] or on the approximate expansion of the scattering wave function in a set of square-integrable basis functions[3] follows from two fundamental facts. First, as the resonance energy belongs to the continuous spectrum of the $(N+1)$-electron Hamiltonian H (the target is assumed to have N electrons), there exists an inherent difficulty in identifying *which* discrete positive eigenvalue of an approximate, finite-rank representative of H corresponds most closely to the metastable state of interest. Second, as the resonance wave function is not square integrable, the computational difficulties in treating such states are potentially more severe than those encountered in the treatment of ordinary bound states (for which highly efficient computer codes are widely available).

A method which eliminates many of these theoretical difficulties follows from a series of theorems due to

Aguilar, Balslev, Combes, and Simon (ABCS).[4] Essentially, these authors consider the spectrum of a modified nonrelativistic Hamiltonian H_θ which is obtained from the true Hamiltonian H by application of a complex scaling transformation. It follows from their analyses that the mathematical description of a resonance can be fundamentally simplified in two respects. First, the spectrum of the transformed Hamiltonian contains, in addition to the ordinary bound state eigenvalues of the untransformed H, complex eigenvalues Z which are related to the resonance energies E and widths Γ by $Z = E - i\Gamma/2$. Second, application of the ABCS transformation makes the resonance wave function square integrable. Thus, this method appears to offer great promise for the determination of accurate resonance energies in a computationally tractable form. In fact, this approach has been successfully applied to atomic[5] and molecular[6] shape resonances within frameworks which, respectively, neglected or included electron correlation effects. Application of the ABCS transformation to the one-electron propagator, which to our knowledge has not previously been realized, is the principal subject of this paper. This approach yields an *ab initio* electron–molecule effective potential (the self-energy or optical potential) which can be systematically improved and which includes electron–electron interactions in a proper manner.

In Sec. II we outline the coordinate rotation technique as applied to the Hamiltonian itself. We there quote the most relevant results of the ABCS theorems related to the spectrum of the Hamiltonian following coordinate rotation. Section III introduces the electron propagator in the form of the superoperator resolvent introduced by Goscinski and Lukman.[7] There we show how the ABCS transformation can be used to obtain a rotated propagator from which resonance information can be extracted in a highly systematic and computationally tractable manner. This is followed in Sec. III by a sketch of the derivation and approximations which lead to a rotated propagator which is correct to second order in the electron–electron interaction. Section IV contains the results of a second order computation of the lowest ^2P shape reso-

nance in the Be anion. Our results are compared with those recently obtained by more approximate *ab initio* (static exchange) and model potential methods.[8] We close with a few brief remarks concerning the directions for future research on this interesting problem.

II. COORDINATE ROTATION AND THE RESOLVENT $(ZI - H)^{-1}$

Much of the motivation for the coordinate rotation technique follows from the desire to treat resonances as electronic states which—through possessing a finite lifetime $\tau > 0$—are nonetheless representable by square-integrable solutions (at complex energy) of a modified form of the Schrödinger equation. The modified Hamiltonian describing such a state is necessarily non-Hermitian. The complex eigenvalue of the resonance is then customarily written in the form $Z = E - i\Gamma/2$ for E, the energy, and $\Gamma = \hbar/\tau$, the width. This decomposition is consistent with the view that the time decay of a resonance is approximately exponential, though it can be shown that this decay cannot be strictly correct for times which are either very short or very long.[9]

In fact, initial applications of the coordinate rotation device involved letting the coordinates in the wave function[10] assume complex values [$r \rightarrow r \exp(i\theta)$], followed by solution of the Schrödinger equation. It is easy to see that one might equivalently rotate the coordinates in the Hamiltonian, but not those in the trial wave function, and attempt solution of the eigenvalue problem $(Z - H_\theta)\Psi_\theta = 0$. The operator H_θ is taken to be the coordinate rotated form of the ordinary Hamiltonian H_0 as

$$H_0 = -\frac{1}{2}\sum_i^{N+1} \nabla_i^2 - Z \sum_i^{N+1} \frac{1}{r_i} + \sum_{i<j}^{N+1} \frac{1}{r_{ij}}, \tag{1}$$

$$H_0 = T_0 + V_0. \tag{2}$$

Replacement of r_i by $r_i \exp(i\theta)$ yields the coordinate rotated Hamiltonian $H_\theta = \exp(-2i\theta)T_0 + \exp(-i\theta)V_0$.

Detailed analyses of the conditions under which the Hamiltonian H_0 can be analytically continued to the complex plane have been given by Aguilar, Balslev, Combes, and Simon,[4] the collected work we shall call the ABCS theorem. The result is a beautiful characterization of the pole structure of the continued $(N+1)$-electron resolvent $(Z - H_\theta)^{-1}$. Rather than prove these theorems here, it is sufficient to quote their results on the spectrum of H_θ. This we do in the form of the following theorem.[4]

Let the Hamiltonian for an $(N+1)$-electron state be defined by $H_\theta = e^{-2i\theta} T_0 + e^{-i\theta} V_0$, a sum of kinetic (T) and potential (V) parts, such that H_θ is analytic on $0 < \theta < \pi/2$. The eigenvalue spectrum $\sigma(\theta)$ of H_θ can be divided into a discrete, point spectrum $\sigma_d(\theta)$ and a continuous spectrum $\sigma_e(\theta)$. Let $\Sigma(\theta)$ be the set of complex thresholds of the $(N+1)$-electron system. (For $\theta = 0$ these correspond to energies of a neutral N-electron parent plus an added electron of arbitrary positive kinetic energy. In what follows it is profitable to think of the thresholds as a series of half-lines beginning at the energy of some state of the parent.) The spectrum of H_θ is composed of the following elements:

(a) a set of real elements in σ_d and Σ: these correspond to the real bound states and thresholds of H_0, and are independent of θ;

(b) an essential spectrum $\sigma_e(\theta)$ which consists of a number of complex rays each making an angle -2θ to the positive real axis: each ray begins at one of the real thresholds of H_0 and may be regarded as a rotating branch cut; in addition to these, there also exists a set of rays which begin at the complex thresholds in $\Sigma(\theta)$; these later also make an angle -2θ to the positive real axis;

(c) a set of nonreal eigenvalues in $\sigma_d(\theta)$ and $\Sigma(\theta)$: these are *defined* to be resonances of the $(N+1)$ electron system with $Z = E - i\Gamma/2$; each resonance eigenvalue lies on a sector or sheet of the complex plane bounded by two of the rays described in part (b); on a given sheet, the resonance eigenvalue is independent of θ.

Thus, one has the following picture of the multi-sheeted eigenvalue spectrum of H_θ (see Fig. 1). At $\theta = 0$ the bound states and thresholds of H_0 appear on the real line (H_0 is Hermitian). However, as the rotation angle θ is increased, several features of the spectrum become apparent: (1) the bound states and thresholds are invariant to the rotation and remain fixed; (2) the esential spectrum of H_0 "fans out" in the complex plane; each complex ray begins at a threshold and rotates, making an angle -2θ to the positive real axis; (3) one sees no isolated complex resonance eigenvalues until $\theta = \theta_{res}$, at which point one appears to become detached from a rotating branch cut. This eigenvalue is then independent of $\theta > \theta_{res}$ until such time as it is passed over by another rotating branch cut beginning at a higher energy threshold. The resonance eigenvalue then "disappears" as one is now on another sheet of the surface defined by the rotating branch cuts.

Of course, the behavior of the eigenvalues which arise in a finite basis (approximate) application of coordinate rotation techniques shows some deviation from this "ideal" behavior.[11] In particular, we wish to take account of the fact that the resonance eigenvalue may depend on a real scale factor α in addition to its dependence on the rotation angle θ. Such a real scale factor is introduced in order to permit convenient variation of the radial "diffuseness" of our orbital basis, and to allow us to require that the state of interest satisfy a virial theorem. Thus, we define the complex parameter $\eta = \alpha \exp(-i\theta)$ for both α and θ real and positive; the coordinate rotated Hamiltonian H_η is then, in second-quantized rotation, given by

$$H_\eta = \sum_{ij} h_{ij}(\eta) c_i^+ c_j + \frac{\eta}{2} \sum_{ijk} \langle ij | kl \rangle c_i^+ c_j^+ c_l c_k, \tag{3}$$

where, for an atom, the matrix dements $h_{ij}(\eta)$ are sums of kinetic and potential energy parts

$$h_{ij}(\eta) = \eta^2 t_{ij}(\eta = 1) + \eta v_{ij}(\eta = 1) \tag{4}$$

and the $\langle ij | kl \rangle$ are two-electron repulsion integrals. (For a molecule, the nuclear attraction matrix elements scale according to $\langle \phi_m | | r - R\eta |^{-1} | \phi_n \rangle$ which is not homogeneous.)

The coordinate rotated resolvent is then $(ZI - H_\eta)^{-1}$. It is analytic in η and also analytic in Z except its complex poles. These latter, when referenced to the separating-computed energy of the N-electron parent, give a resonance energy and width which is stationary provided the parameter η is chosen to satisfy $\partial Z/\partial \eta = 0$. Equivalently, the optimum approximate resonance eigenvalue satisfies the system of equations below:

$$\frac{\partial Z}{\partial \alpha} = \frac{\eta}{\alpha} \frac{\partial Z}{\partial \eta} = 0 , \qquad (5a)$$

$$\frac{\partial Z}{\partial \theta} = -i\eta \frac{\partial Z}{\partial \eta} = 0 . \qquad (5b)$$

These latter equations constitute a complex form of the virial theorem.[11] Their use in the approximate application of the coordinate rotation method is essential, a point to which we shall later return.

III. COORDINATE ROTATION OF THE SUPEROPERATOR RESOLVENT $(Z\hat{I} - \hat{H})^{-1}$

It is by now widely appreciated[12-15] that the ionization potentials and electron affinities of an N-electron system can be obtained from the (real) poles of the one-electron propagator, or reduced Green's function $\mathbf{G}(E)$. Let the exact ground state of the parent atom or molecule be designated by $|{}^N_0\rangle$ and $C_i(\tau)$ and $C_j^+(0)$ be fermion annihilation and creation operators in the Heisenberg representation for times τ and $\tau = 0$, respectively. Then, with the Heaviside step function $\theta(\tau)$, one defines[14] the electron propagator $\overline{\mathbf{G}}(\tau)$ through the matrix elements in

$$\overline{G}_{ij}(\tau) = -i\theta(\tau)\langle{}^N_0 | C_i(\tau) C_j^+(0) | {}^N_0\rangle$$
$$+ i\theta(-\tau)\langle{}^N_0 | C_j^+(0) C_i(\tau)|{}^N_0\rangle , \quad i,j = 1,2,\ldots,P . \qquad (6)$$

The Fourier transform $\mathbf{G}(E)$ of $\overline{\mathbf{G}}(\tau)$ is then defined by

$$\mathbf{G}(E) = \lim_{\delta \to 0^+} \int_{-\infty}^{\infty} d\tau \exp[i(E \pm i\delta)\tau]\overline{\mathbf{G}}(\tau) , \qquad (7)$$

in which the $\pm$ sign on the positive infinitessimal δ is chosen to guarantee convergence of the right hand side. Insertion of a complete set of $(N \pm 1)$-electron states $|{}^{N\pm1}_\mu\rangle$ in Eq. (6) followed by taking the Fourier transform and the limit as $\delta \to 0$ yields the spectral representation of $\mathbf{G}(E)$:

$$G_{ij}(E) = \sum_\mu \frac{\langle {}^N_0 | C_i(0)|{}^{N+1}_\mu\rangle\langle{}^{N+1}_\mu | C_j^+(0)|{}^N_0\rangle}{E + (E^N_0 - E^{N+1}_\mu)}$$
$$+ \sum_{\mu'} \frac{\langle{}^N_0 | C_j(0)|{}^{N-1}_{\mu'}\rangle\langle{}^{N-1}_{\mu'}|C_i(0)|{}^N_0\rangle}{E + (E^{N-1}_{\mu'} - E^N_0)} . \qquad (8)$$

The poles of $\mathbf{G}(E)$ thus occur at the energy differences $E = E^{N+1}_\mu - E^N_0)$ and $E = (E^N_0 - E^{N+1}_\mu)$, which are, respectively, the *negatives* of the electron affinities and ionization potentials of the N-electron parent.

This property of $\mathbf{G}$ is particularly relevant to the discussion of metastable anions, since the coordinate-rotated propagator $\mathbf{G}(Z, \theta)$ exhibits a *complex* electron affinity at a resonance, i.e., the eigenvalue spectrum of the coordinate-rotated propagator assumes the same form as that given in Fig. 1, with the exception that the eigenvalues correspond to energy *differences* between
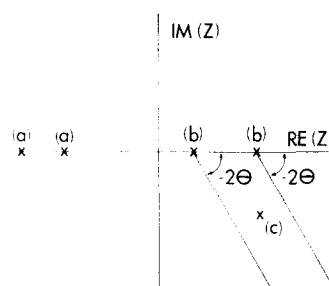

FIG. 1. Schematic view of the eigenvalue spectrum of H_θ: (a) bound states; (b) real thresholds; (c) resonance.

N and $N \pm 1$ electron states. As θ is increased above zero, the bound target to bound ion energy differences remain unaffected whereas complex eigenvalues located in sectors between adjacent branches of the essential spectrum can be uncovered at θ_{res}. The resonance eigenvalue is then

$$Z_{res} = \Delta E_{res} - i\Gamma_{res}/2$$
$$= (E^{ion}_{res} - E_{parent}) - i\Gamma^{ion}_{res}/2 \qquad (9)$$

since the stable target has zero width. Scaling the propagator, it follows that a computation performed on the neutral parent yields information on the resonance state of interest. Of course, Eq. (8) does not represent a computationally useful form of the propagator since its use requires knowledge of all the $(N \pm 1)$-electron eigenstates.

The propagator can be put into a computationally tractable form by writing it in the form of the superoperator resolvent introduced by Goscinski and Lukman.[7] To achieve this, we introduce the superoperators $\hat{I}$ and $\hat{H}$ which for an arbitrary operator X satisfy

$$\hat{I}X = X , \qquad (10a)$$

$$\hat{H}X = [X, H]_- . \qquad (10b)$$

We also introduce the binary product $(A | B)$ defined with respect to the reference wave function $|{}^N_0\rangle$ by[16]

$$(A | B) = \langle{}^N_0 | [A^+, B]_+ |{}^N_0\rangle . \qquad (11)$$

By use of the identity

$$e^{iHt} X e^{-iHt} \equiv e^{-i\hat{H}t} X , \qquad (12)$$

which is valid for all operators X and H, Eq. (6) may be written in the following form:

$$G_{ij}(\tau) \equiv -i\theta(\tau)\langle{}^N_0 | [e^{-i\hat{H}\tau} C_i(0)] C_j^+(0) |{}^N_0\rangle$$
$$+ i\theta(-\tau)\langle{}^N_0 | C_j^+(0)[e^{-i\hat{H}\tau}C_i(0)] |{}^N_0\rangle . \qquad (13)$$

Finally, collection of the operators c_i into a column vector $\mathbf{C}$ and use of Eq. (12) allows the energy-dependent propagator to be written compactly as

$$\mathbf{G}(E) = (\mathbf{C} | (E\hat{I} - \hat{H})^{-1}|\mathbf{C}) . \qquad (14a)$$

The coordinate rotated version of this propagator is clearly

$$\mathbf{G}(Z, \eta) = (\mathbf{C} | (Z\hat{I} - \hat{H}_\eta)^{-1}|\mathbf{C}) , \qquad (14b)$$

which is defined for the superoperator form of the Hamilto-

nian in Eq. (3). These latter equations provide a convenient starting point for an order-by-order analysis of the propagator by perturbation and partitioning techniques.[17] This we now consider.

In formulating a set of equations in terms of which $\mathbf{G}(Z, \eta)$ can be computed it is convenient to assume, as in conventional Green's function developments,[14,15] that we have available as a basis the real Hartree–Fock (HF) spin orbitals ϕ_i and orbital energies ϵ_i, as well as the two-electron integrals $\langle ijkl \rangle$ of the target's unrotated HF Hamiltonian. The single configuration HF determinant of the (assumed closed shell) target is represented by the symbol $|0\rangle$. The true target rotated wave function $|{}_0^N\rangle$ is assumed to be expressed as $|{}_0^N\rangle \equiv [|0\rangle + |\Psi^1\rangle] S^{-1/2}$, where S is the normalization constant and $|\Psi^1\rangle$ involves electron correlation and coordinate-rotation effects. The coordinate-rotated Hamiltonian H_η defined in Eq. (3) is (for use in subsequent perturbation analysis) expressed in the form H^0 (the HF target Hamiltonian) plus the remainder H_η^1. H_η^1 contains both the coordinate rotation and correlation effects $(V_\eta - V_{\mathrm{HF}})$ as well as the difference between the rotated and unrotated Hartree–Fock operators $[h_{\mathrm{HF}}(\eta) - h_{\mathrm{HF}}(\eta = 1)]$. We remark at this point that we have no proof of the convergence of this perturbation scheme though its merits are discussed more fully below.

We use Greek indices $\alpha, \beta, \ldots$ to label the occupied single-particle states in $|0\rangle$ while $p, q, \ldots$ label the unoccupied levels $p = N+1, N+2, \ldots, P$. Further, we let $i, j, k,$ and l be index arbitrary (occupied or unoccupied) levels. The normalized first-order wave function arising from Rayleigh–Schrödinger perturbation theory is then

$$|{}_0^N\rangle = S^{-1/2}\left[1 + \sum_\alpha k_\alpha^p(\eta)\, p^+\alpha + \eta \sum_{\substack{\alpha < \beta \\ p < q}} \frac{\langle pq \| \alpha\beta \rangle\, p^+ q^+ \beta\alpha}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q}\right]|0\rangle .$$

(15)

The normalization coefficient S is

$$S = 1 + \sum_{\alpha p}\left[k_\alpha^p(\eta)\right]^2 + \eta^2 \sum_{\substack{\alpha < \beta \\ p < q}} \frac{|\langle pq \| \alpha\beta \rangle|^2}{(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)^2}$$

(16)

and the complex coefficients $k_\alpha^p(\eta)$ are those determined by first order Rayleigh–Schrödinger perturbation theory

$$k_\alpha^p(\eta) \equiv \frac{\epsilon_{\alpha p}(\eta)}{\epsilon_\alpha(1) - \epsilon_p(1)} .$$

(17)

The quantity $\epsilon_{\alpha p}(\eta)$ is an element of the complex symmetric "Fock matrix"

$$\epsilon_{\alpha p}(\eta) \equiv h_{\alpha p}(\eta) + \eta \sum_\sigma \langle \sigma\alpha \| \sigma p \rangle ,$$

(18)

and the ϵ's in the denominator are the real elements of the diagonal Fock matrix $(\eta = 1)$ in the absence of any coordinate rotation. The coefficients $k_\alpha^p(\eta)$ clearly arise from the coordinate rotation alone. The other two-electron integral terms in Eq. (15) enter as a result of both coordinate rotation and correlation effects.

Following the conventional operator-based derivation,[18] one next introduces a complete set of ionization operators $\mathbf{h} = \{h_1, h_3, h_5, \ldots\}$ which satisfy the commutation rules for fermions, and which act on an arbitrary ket

to change its electron number by plus or minus one. A typical element of h_1 is a single annihilation operator c_i, while a typical element of h_{2j+1} is a product of $2j + 1$ such operators, e.g.,

$$h_3^{(1)} = \{c_\alpha^+ c_p c_q \mid \alpha < p < q\} ,$$

(19a)

$$h_3^{(2)} = \{c_r^+ c_\beta c_\mu \mid r > \beta > \mu\} .$$

(19b)

The operators in $h_3^{(1)}$ act to the left, creating an $(N+1)$-electron state from an N-electron one; those in $h_3^{(2)}$ operate to the right to create an $(N-1)$-electron state from an N-electron one. These operators can then be collected into a set $\mathbf{q}$, Schmidt orthogonalized with respect to the binary product $(A|B)$ defined earlier relative to the first order wave function of Eq. (15). The resulting first order normalized operators q_1 and q_3 are

$$q_1 = \{c_i \mid i = 1, 2, 3, \ldots, P\} ,$$

(20a)

$$q_3^{(1)} = \{c_\alpha^+ c_p c_q - k_\alpha^p(\eta)\, c_q + k_\alpha^q(\eta)\, c_p \mid \alpha < p < q\} ,$$

(20b)

$$q_3^{(2)} = \{c_r^+ c_\beta c_\mu - k_\beta^r(\eta)\, c_\mu + k_\mu^r(\eta)\, c_\beta \mid r > \beta > \mu\} .$$

(20c)

The desired, second order, propagator can be shown[13,15] to be expressible in the form

$$\mathbf{G}^{-1}(Z, \eta) = [Z\mathbf{I} - \mathbf{A} - \mathbf{B}\mathbf{M}^{-1}\mathbf{C}] ,$$

(21)

in which the matrices $\mathbf{A}$, $\mathbf{B}$, $\mathbf{M}$, and $\mathbf{C}$ are defined as follows:

$$\mathbf{A} = (q_1 | \hat{H}_\eta | q_1) ,$$

(22a)

$$\mathbf{B} = (q_1 | \hat{H}_\eta | q_3) ,$$

(22b)

$$\mathbf{M} = (q_3 | (Z\hat{I} - \hat{H}_\eta) | q_3) ,$$

(22c)

$$\mathbf{C} = (q_3 | H_\eta | q_1) .$$

(22d)

The explicit form of the coordinate-rotated matrix elements as they were used in the calculations discussed in the next section is given in the Appendix.

Alternately, one may think of the above expression for $\mathbf{G}^{-1}$ as being given in terms of the one-electron effective Hamiltonian $\mathbf{L}(Z, \eta)$:

$$\mathbf{G}^{-1}(Z, \eta) = Z\mathbf{I} - \mathbf{L}(Z, \eta) ,$$

(23)

in which

$$\mathbf{L}(Z, \eta) \equiv \mathbf{A} + \mathbf{B}\mathbf{M}^{-1}\mathbf{C} .$$

(24)

The poles of this approximate $\mathbf{G}$ occur at the zeros of $\mathbf{G}^{-1}$, and are thus (for fixed η) the energy-dependent eigenvalues of the equation

$$\mathbf{L}(Z_\beta, \eta)\, \Phi(Z_\beta) = Z_\beta\, \Phi(Z_\beta) , \quad \beta = 1, 2, \ldots, P .$$

(25)

In practice, this last equation is solved by iteration. One begins with a guess $Z_\beta^{(1)}$ of the resonance eigenvalue, constructs the matrix $\mathbf{L}(Z_\beta^{(1)}, \eta)$, and solves the determinantal equation

$$\det[Z\mathbf{I} - \mathbf{L}(Z, \eta)] = 0$$

(26)

for a new approximation $Z_\beta^{(2)}$, and so on. Since $Z_\beta^{(i)}$ is complex, we choose $Z_\beta^{(i+1)}$ such that it is the eigenvalue of $\mathbf{L}$ which lies closest to $Z_\beta^{(i)}$ in the complex plane in the sense that $|Z_\beta^{(i+1)} - Z_\beta^{(i)}| = \min$. It has been our experience that convergence of the above sequence can be obtained in three or four iterations with a tolerance τ set at $\tau = 1 \times 10^{-4}$ a.u. This value of τ was used in all calculations reported below.

IV. APPLICATION TO ^2P Be$^-$

As an illustrative test of the methods outlined above we chose to study the ^2P shape resonance in the ground state of the Be atom. The atom was chosen because our Green's function development is, thus far, restricted to closed shell targets and because of the relatively small size of this atom (which results in low computational expense). Shape resonances have been experimentally observed[19] in the group IIA metals and their transition metal analogs Zn, Cd, and Hg. Thus, the simpler Be atom may be expected to show such resonance behavior at low energy. Moreover, although no experimental measurements of possible resonance behavior have been made for Be, this atom has been studied by a variety of theoretical techniques.

The first calculation on the ^2P state of Be$^-$ which made use of complex coordinate methods was carried out by Rescigno, McCurdy, and Orel[8] with the results given in Table II. These authors begin with a single Hartree–Fock calculation on the neutral parent for which

$$\Psi = \hat{A}[\phi_{1s}\bar{\phi}_{1s}\phi_{2s}\bar{\phi}_{2s}] \ . \tag{27}$$

They next form a square integrable approximation to the $(N+1)$-electron Hamiltonian by employing a basis of real configurations Γ_k defined by

$$\Gamma_k \equiv \hat{A}[\phi_{1s}\bar{\phi}_{1s}\phi_{2s}\bar{\phi}_{2s}\phi_{kp}] \tag{28}$$

and expanding H^{N+1} in terms of an approximate spectral resolution,

$$H^{N+1} \approx \sum_{kl} |\Gamma_k\rangle\langle\Gamma_k|H|\Gamma_l\rangle\langle\Gamma_l| \ . \tag{29}$$

The orbitals ϕ_{kp} are formed by Schmidt orthogonalizing a set of primitive Slater-type basis functions. The complex resonance wave function is then expanded in terms of the set of antisymmetric functions $\chi_i(\theta)$:

$$\chi_i(\theta) \equiv \hat{A}[\phi_{1s}\bar{\phi}_{1s}\phi_{2s}\bar{\phi}_{2s}\phi_{ip}(r\,e^{i\theta})] \ . \tag{30}$$

TABLE I. Basis, ground-state energy, and ionization potential obtained for neutral Be parent.

Orbital	Exponents/coefficients			[5s, 7p]
1s	1264.5857	189.9368	43.1590	12.0987
	3.8063	1.2729/		
	0.001945	1.014835	0.072090	0.237154
	0.469199	1.356520		
2s	0.7478 /	1.		
3s	0.2200 /	1.		
4s	0.0823 /	1.		
5s	0.0300 /	1.		
1p	3.1965	0.7470	0.2200/	
	0.05570	0.261551	0.793792	
2p	0.0800 /	1.		
3p	0.0500 /	1.		
4p	0.0300 /	1.		
5p	0.0125 /	1.		
6p	0.0080 /	1.		
7p	0.0031 /	1.		

Total energy (a.u.) = -14.566812
Ionization potential (a.u.)
   Present = 0.320
   Doll and Reinhardt = 0.327
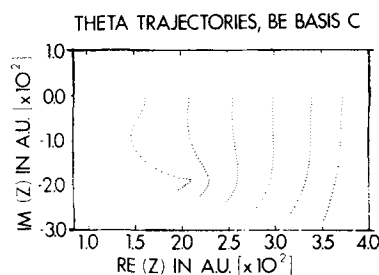

THETA TRAJECTORIES, BE BASIS C

FIG. 2. A collection of θ trajectories for the basis listed in Table I. From left to right, the $\alpha = 0.75$, 0.80, 0.85, 0.90, 0.95, 1.0. The θ increment is 0.01 rad, beginning at $\theta = 0.0$ and ending at $\theta = 0.35$ rad.

Finally, the complex rotated Hamiltonian matrix $\mathbf{H}_\theta$ is formed according to

$$(H_\theta)_{ij} = \sum_{mn}\langle\chi_i(\theta)|\Gamma_m\rangle\langle\Gamma_m|H|\Gamma_n\rangle\langle\Gamma_n|\chi_j(\theta)\rangle \ , \tag{31}$$

$$\mathbf{H}_\theta \equiv \hat{\mathbf{S}}_\theta\mathbf{H}\mathbf{S}_\theta \ .$$

There are two differences between this procedure and a full coordinate-rotation calculation. First, the above authors rotate only the coordinates in the "active" p-orbital space, and second, they approximate H with a finite spectral representation. As a result, the complex eigenvalues Z_k of $\mathbf{H}$ defined in Eq. (31) depend on the rotation angle through the complex overlap integrals $\langle\chi_i(\theta)|\Gamma_m\rangle$, while the matrix $\mathbf{H}$ is independent of θ.

In our work on Be, we begin by computing the zeroth order Hartree–Fock wave function in the basis of Gaussian-type functions listed in Table I; the corresponding ground-state energy of ^1S Be and the first ionization potential are also listed in Table I. Our method for finding the value of the complex scale η at which Eqs. (5) are obeyed is as follows: As is common in the literature on this subject, we refer to a "θ trajectory" as the locus points $Z_\alpha(\theta)$ in the complex plane for fixed α. Likewise, we refer to an "α trajectory" as the locus of points $Z_\theta(\alpha)$ for fixed θ. Then, for fixed $\alpha = \alpha_1$ there exists at least one point at which Eq. (5b) will be satisfied provided the basis is adequate to represent the resonance. A family of θ trajectories for the ^2P Be$^-$ resonance is plotted in Fig. 2 for various values of the real scale α.

Examination of the figure indeed confirms the strong dependence of the resonance eigenvalue on both the rotation angle θ and real scale α. In fact, for the choice $\alpha = 1.0$ (i.e., using the original atomic orbital basis chosen in a more or less arbitrary fashion), the resonance eigenvalue exhibits the same behavior as a typical nonresonant root! Thus, in finite basis calculations the precise location of the resonance root is critically dependent on both the overall basis scale and on the rotation angle. Following these trajectory calculations, we then applied a complex Newton–Rhapson iteration to the function $Z' \equiv \partial Z/\partial\eta$ in order better to locate its (complex) zero. The derivatives Z' and Z'' were computed analytically (this is permissible since $\mathbf{L}$ can easily be differentiated with respect to η), and the converged value of the resonance eigenvalue was found to be

TABLE II. Resonance parameters computed for ^2P Be.

	E (eV)	Γ (eV)
Rescigno, McCurdy, and Orel (Ref. 8)	0.76	1.11
Hunt and Moiseiwitsch (Ref. 8)	0.60	0.22
Kurtz and Öhrn (Ref. 8)		
Static exchange	0.77	1.61
Static exchange plus polarization	0.20	0.28
Present	0.57	0.99

$Z = (2.0968 \times 10^{-2}, -1.8142 \times 10^{-2}$ a. u.) at $\alpha = 0.73822$, $\theta = 0.25031$ rad. Here the first derivative had the value $Z' = (-1.8697 \times 10^{-5}, 2.7817 \times 10^{-5})$ with magnitude 3.3517×10^{-5}. Thus, the second-order Green's function estimate of the resonance parameters gives a stable eigenvalue Z for which the energy and width are $E = 0.57055$ eV, $\Gamma = 0.98732$ eV.

Other, more approximate static exchange computations of the resonance parameters of ^2P Be⁻ have been carried out by Kurtz and Öhrn,[8] who used the Harris–Michels[20] method followed by analysis of the $l = 1$ phase shift. The results of these computations are given in Table II, from which it can be seen that the resonance energies computed by this method are in good agreement with the static exchange values obtained via the complex coordinate calculation of Rescigno et al.[9] The agreement between the calculated widths, however, is less satisfactory, which may be due to the broadness of the resonance and the fitting procedures used by Kurtz and Öhrn in determining the width from the phase shift.

Because the atoms of Group II are highly polarizable, the inclusion of higher-order terms absent at the static-exchange level should be important. Such computations were carried out by Kurtz and Öhrn, and by Hunt and Moiseiwitsch.[8] Both pairs of authors add to the static exchange potential a polarization term which is dependent on an arbitrary cutoff parameter; the resulting dramatic shift in the resonance parameters can be seen in Table II. The resonance widths computed by the two methods are again in relatively poor agreement with one another. One reason for this might be due to the fact that the Kurtz–Öhrn polarization potential has a physically reasonable long-range part which is not included in the polarization potential used by Hunt and Moisewitsch. Both these methods are critically dependent on the cutoff parameter r_0, which makes interpretation of the computed resonance parameters difficult.

The second-order results obtained in the present work are also listed in Table II, for the basis set listed in Table I. As might be expected, the effects of correlation and target polarization combine to reduce both the energy and width of the ^2P Be⁻ resonance compared to the static exchange values. Significantly, it would appear that the reduction in these parameters is greatly exaggerated by the more approximate static exchange plus polarization calculations, though again the dependence of these last methods on the cutoff parameter r_0 makes an assessment of the accuracy of the computed values difficult. Based upon our experience with using

second and third order Green's functions to compute electron affinities involving bound anions, we expect the second order results to be in error by 0.3–0.6 eV. Hence, we are in no position to claim that our calculated E and Γ are more accurate than those of Kurtz and Öhrn. An objective comparison must await the results of a high order Green's function study as well as an accurate experimental determination.

V. SUMMARY AND CONCLUSIONS

In the research presented here we have shown how one can employ the coordinate rotation technique, which has been used previously by others within a wave function framework, to obtain a modified one-electron propagator $\mathbf{G}(Z,\eta)$ or effective one-electron Hamiltonian $\mathbf{L}(Z,\eta)$. We have, for a closed-shell target, given expressions in terms of the target Hartree–Fock orbitals and orbital energies, which permit $\mathbf{L}(Z,\eta)$ to be evaluated through second order in the electron–electron interaction. The complex poles Z_β of $G(Z,\eta)$ which are stable over some range of rotation angles $(\theta > \theta_{res})$ give the shape resonance energies and widths $Z = E_\beta - i\Gamma_\beta/2$ relative to the total energy of the target atom.

We have applied this second order coordinate rotated Green's function method to study the ^2P shape resonance of Be⁻, obtaining $E_{res} = 0.57$ eV, $\Gamma_{res} = 0.99$ eV. These values were compared to the results of the coordinate-rotation wave function calculations which employed the static exchange HF) electron–atom potential as well as to those of phase shift calculations which used model static-exchange plus cutoff polarization potentials.

Unfortunately, an experimental evaluation of the resonance energy of Be⁻ is not yet available; thus, it is not possible to give a more critical evaluation of the accuracy of the results obtained by the rotated Green's function method. It is, however, quite clear that the Green's function approach as outlined and utilized above suffers from (at least) the following drawbacks:

(1) The fact that $\mathbf{G}(Z,\eta)$ is obtained only through second order in the electron interaction severely limits the precision with which E and Γ can be computed. This judgement is based upon an experience with Green's function calculations of atomic and molecular electron affinities. We are presently undertaking a full third order treatment of $\mathbf{G}(Z,\eta)$ to remedy this situation.

(2) Treatment of the effects of rotation on the target wave function via perturbation theory may not be adequate if α is greater than unity or if θ is large. To overcome this potential problem, one could employ as a spin orbital basis (in terms of which the unperturbed H^0 is defined) the rotated HF Hamiltonian. Then the K_α^η would vanish and $\mathbf{L}(Z,\eta)$ would be given by the same expressions which arise in the conventional (unrotated) Green's function, except that the HF orbitals and orbital energies would be complex and η dependent. Thus, as η is varied, the rotated HF problem would have to be solved again, and construction of the HF-orbital two-electron integrals $\langle ij | kl \rangle$ needed to compute $\mathbf{L}$ would involve a complex integral transformation; this could be quite time consuming! Alternatively, if in the iterative

search for a stable resonance root α becomes large, one could simply scale all of the atomic basis orbitals by this value of α, with $\theta = 0$, to obtain a *new* starting basis with which to carry out a new HF calculation. The new HF orbitals could then be used to begin a new search for a stable resonance root.

(3) The assumption that the target in a closed-shell species whose wave function is adequately approximated as a HF configuration augmented by a first order Rayleigh–Schrödinger correction severely limits the systems to which our tools can be applied. In fact, this assumption is especially unsuited in the case of the highly correlated Be atom. The extension of our developments to correlated targets, for which the perturbation-theory wave function is not accurate, is under our active consideration.

In spite of these obvious limitations in the Green's function method as it is presently constituted, we feel that the use of the approach advocated here offers a computationally tractable alternative to $(N + 1)$-electron wave function methods. In fact, the Green's function technique seems to have potential advantages over wave function-based approaches:

(1) The present framework offers a mechanism for computing the coordinate rotated version of the true one-electron effective Hamiltonian $L(Z, \eta)$ which can be systematically improved (by augmenting the q_k space and improving the quality of the target wave function) so that it includes higher order electron interaction effects. The ability to compute and analyze the structure of such an energy-dependent, nonlocal effective potential suggests the possibility of developing deeper physical insight as well as new physical models for the electron–target interaction process.

(2) Because the poles of the Green's function yield directly the energy differences between $(N + 1)$- and N-electron states, it is likely that spurious effects arising from rotating the target's core electrons, which have been observed to cause substantial numerical difficulties in coordinate rotated wave function studies, are eliminated or at least reduced. In fact, it was precisely these difficulties which motivated Rescigno *et al.*[8] to develop a model in which only the coordinate of the active orbital is rotated. Of course, in a complete basis description, the rotation of H should have no effect on the bound states, and hence within the HF picture this should not affect the target's occupied HF orbital energies. However, the use of finite atomic orbital bases gives rise to some (spurious) θ dependence of the occupied orbital energies, which shows up as a spurious θ dependence of the total electronic energy of the target-plus-electron system as computed in a wave function approach. The Green's function by analytically subtracting the target's energy, allows only the θ dependence of the resonance energy to be evaluated.

The energy dependent one-electron effective potential defined by $L(E, \eta = 1)$ could, following Rescigno, McCurdy, and Orel,[8] be used to define a "semirotated" optical potential whose matrix elements in the rotated orbital basis $\{\phi_i(\mathbf{r} \exp(i\theta))\}$ are defined by $\tilde{L}_{ij}(E)$

$$\equiv \sum_{kl} \langle \phi_i(\mathbf{r} \exp(i\theta)) | \phi_k(\mathbf{r}) \rangle L_{kl}(E) \langle \phi_l(\mathbf{r}) | \phi_j(\mathbf{r} \exp(i\theta)) \rangle.$$ In this manner, the unrotated $L(E)$ in the HF basis is used and the only effect of rotation is contained in the overlap integrals just as is the case in the work of Rescigno *et al.*[8] This approximation to the "correctly rotated" $L(Z, \eta)$ is worthy of further study.

It is our feeling that the *ab initio* one-electron effective potential approach advocated here merits a great deal of further consideration. We plan to explore the applications of this method as it now stands to a wide range of molecular targets. We also plan the inclusion of higher order electronic interactions which will permit the study of open-shell and highly correlated (multiconfigurational) targets.

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APPENDIX

Rather than give a complete expansion of the terms in the matrices **A**, **B**, **M**, and **C** we focus on the means by which all terms of second or lower order can be obtained. (A treatment of the unrotated form of the propagator correct to second order was first given by Doll and Reinhardt.[15]) The important element which must be kept in mind here is that both the ground state wave function $|\stackrel{N}{_0}\rangle$ *and* the operators q_1, q_3 contain zeroth and first order parts. Furthermore, failure to adequately deal with this fact leads to a nonsymmetric contribution **BM**$^{-1}$**C** such as that considered by Nehrkorn, Purvis, and Öhrn.[21]

To obtain all second (or lower) order contributions to **G**$^{-1}$ we expand each of the matrices in Eq. (21) in a sum, appending a superscript whose value is the order of that part of the total Hamiltonian operator whose expectation value is being computed. We also append two subscripts which indicate the order of the left and right wave function component with respect to which the expectation value is to be computed. Note especially that since the operators in **q** contain both zeroth and first order parts, the sum of the sub- and superscripts gives the *minimum* order of a given contribution to the total matrix element.

The matrix A gives the sum of terms

$$\mathbf{A} = (H^0)_{00} + (H^0)_{01} + (H^0)_{10} + (H^0)_{11}$$
$$+ (H_\eta - H^0)^1_{00} + (H - H^0)^1_{01} + (H_\eta - H^0)^1_{10} + 0(3) . \quad (A1)$$

This case is especially simple since the operators in q_1 have only zeroth order parts. Thus, there is a cancellation of terms which leads to the simple, second order result

$$\mathbf{A} = (q_1 | \hat{H}^0 | q_1)_{11} + (q_1 | \hat{H}_\eta | q_1)_{00} + (q_1 | \hat{H}_\eta | q_1)_{01} + (q_1 | \hat{H}_\eta | q_1)_{10} . \quad (A2)$$

The subscripts again indicate the particular components of the normalized wave function $|\stackrel{N}{_0}\rangle = |0\rangle + |\Psi^1\rangle$ with respect to which a given term is to be computed.

A similar result holds for the matrix **M**, which needs to be computed only in zeroth order, since the matrices **B** and **C** themselves begin at first order, as is shown below. Because all off-diagonal elements of **M** are at least first order, it is consistent to retain only the diagonal elements. Thus, the correct matrix **M** is

$$\mathbf{M} = \text{diag}\{(h_3 \,|\, (Z\hat{I} - \hat{H}^0) \,|\, h_3)\} \ . \tag{A3}$$

In a second order treatment of the resonance parameters, the matrix **M** is hence independent of the coordinate rotation η because only H^0 contributes. This leaves the matrices **B** and **C**, which must be handled with some care.

The matrix **B**, which need be computed only in first order in this cae, is the sum

$$\mathbf{B} = (H^0)_{00} + (H^0)_{01} + (H^0)_{10} + (H_\eta - H^0)^1_{00} \ . \tag{A4}$$

Unlike the previous cases, there is only partial cancellation of the first and last terms here. This follows from the fact that the first term contains both zeroth and first order terms (these latter come from the first order part of q_3) whereas the last term $(H_\eta - H^0)^1$ can be consistently computed only by including just the zeroth order part of q_3. (This follows since the operator $H_\eta - H^0 \equiv H^1_\eta$ is by definition first order.) Explicitly, one obtains the first order result

$$\mathbf{B} = (q_1 \,|\, \hat{H}^0 \,|\, q_3)_{00} + (q_1 \,|\, \hat{H}^0 \,|\, h_3)_{01} + (q_1 \,|\, \hat{H}^0 \,|\, h_3)_{10} + (h_1 \,|\, \hat{H}_\eta \,|\, h_3)_{00}$$
$$- (h_1 \,|\, \hat{H}^0 \,|\, h_3)_{00} \ , \tag{A5}$$

which shows clearly the partial cancellation between the first and last terms.

Analysis of the matrix **C** is parallel to that given for **B**. One thus has, for the second order rotated propagator in which the matrix **M** is approximated by its diagonal, the explicit expression

$$G^{-1}_{mn} = Z\delta_{mn} - a_{mn} - \sum_{\alpha < p < q} B_{m,\alpha pq} M^{-1}_{\alpha pq,\alpha pq} C_{\alpha pq,n}$$
$$- \sum_{r > \beta > \mu} B_{m,r\beta\mu} M^{-1}_{r\beta\mu,r\beta\mu} C_{r\beta\mu,n} \ . \tag{A6}$$

The matrix elements appearing in Eq. (A6) are then explicitly given by

$$A_{mn} = \epsilon_{mn}(\eta) + \eta \sum_{\alpha p} k^p_\alpha(\eta) [\langle \alpha m \,|\, pn \rangle - \langle \alpha m \,|\, np \rangle]$$
$$+ \eta \sum_{\alpha p} k^p_\alpha(\eta) [\langle pm \,|\, \alpha n \rangle - \langle pm \,|\, n\alpha \rangle] \tag{A7}$$

$$B_{m,\alpha pq} = -\eta [\langle pq \,|\, \alpha m \rangle - \langle pq \,|\, m\alpha \rangle] \ , \tag{A8}$$

$$B_{m,r\beta\mu} = -\eta [\langle \mu\beta \,|\, rm \rangle - \langle \mu\beta \,|\, mr \rangle] \ , \tag{A9}$$

$$M^{-1}_{\alpha pq,pq} = [Z + \epsilon_{\alpha\alpha}(1) - \epsilon_{pp}(1) - \epsilon_{qq}(1)]^{-1} \ , \tag{A10}$$

$$M^{-1}_{r\beta\mu,r\beta\mu} = [Z + \epsilon_{rr}(1) - \epsilon_{\beta\beta}(1) - \epsilon_{\mu\mu}(1)]^{-1} \ , \tag{A11}$$

$$C_{\alpha pq,n} = -\eta [\langle n\alpha \,|\, pq \rangle - \langle n\alpha \,|\, qp \rangle] \ , \tag{A12}$$

$$C_{r\beta\mu,n} = -\eta [\langle nr \,|\, \beta\mu \rangle - \langle nr \,|\, \mu\beta \rangle] \ . \tag{A13}$$

These lead to a formula for the rotated, second order propagator which is identical in form to the second order propagator previously given by Doll and Reinhardt.[15] To obtain our formula from theirs one simply multiplies each two-electron integral by the complex scale factor

η, followed by making the replacement of their ΔV_{ij} by our $[\epsilon_{ij}(\eta) - \epsilon_{ij}(\eta = 1)]$.

Quite recently, Winkler[22] has attempted to formulate a coordinate-rotated version of the one-particle Green's function, although he has not yet published any computational results. His expression for **G** appears to differ from those presented here because they are expressed in terms of (rotated) HF orbitals which obey $[-\frac{1}{2} \exp(-i2\theta)\nabla^2 - \exp(-i\theta)(Z/r) + \exp(-i\theta)\sum_\alpha (J_\alpha - K_\alpha)]\phi_j = \epsilon_j \phi_j$. The fact that these orbitals and orbital energies are θ dependent means that the two-electron integrals appearing in **L** involve complex orbitals, and hence a complex two-electron integral transformation is required for each θ value. Moreover, the iterative solution of the above rotated HF equations must be repeated for each θ. These two facts make the construction of the Green's function a very expensive (computer time) venture. For these reasons, we have chosen to formulate our **G** in terms of an unperturbed Hamiltonian involving unrotated HF orbitals. This choice then gives rise to a one-electron component to our perturbation $(H_\eta - H^0)$ which thereby introduces factors into our final expression for **G** which are absent from the analogous unrotated Green's function equations.

[1] G. J. Schulz, Rev. Mod. Phys. **45**, 328 (1973); **45**, 423 (1973).

[2] D. G. Truhlar, in *Modern Theoretical Chemistry*, edited by G. A. Segal (Plenum, New York, 1977), Vol. 8.

[3] A. U. Hazi and H. S. Taylor, Phys. Rev. A **1**, 11 (1970).

[4] D. J. Aguilar and J. Combes, Commun. Math. Phys. **22**, 269 (1971); E. Balslev and J. Combes, *ibid.* **22**, 280 (1971); B. Simon, *ibid.* **27**, 1 (1972).

[5] See, for example, T. N. Rescigno, C. W. McCurdy, Jr., and A. E. Orel, Phys. Rev. A **17**, 1931 (1978); G. D. Doolen, J. Nuttall, and C. J. Whery, Phys. Rev. Lett. **40**, 313 (1978); J. J. Wendoloski and W. P. Reinhardt, Phys. Rev. A **17**, 195 (1978); B. R. Junker, Int. J. Quantum Chem. **14**, 372 (1978) and references therein.

[6] N. Moiseyev and C. T. Corcoran, Phys. Rev. A **20**, 814 (1979); C. W. McCurdy, Jr. and T. N. Rescigno, Phys. Rev. Lett. **41**, 1346 (1978).

[7] O. Goscinski and B. Lukman, Chem. Phys. Lett. **7**, 573 (1970).

[8] J. Hunt and B. L. Moiseiwitsch, J. Phys. B **3**, 892 (1970); H. A. Kurtz and Y. Öhrn, Phys. Rev. A **19**, 43 (1979); T. N. Rescigno, C. W. McCurdy, Jr., and A. E. Orel, Phys. Rev. A **17**, 1931 (1978).

[9] B. Simon, Int. J. Quantum Chem. **14**, 529, (1978).

[10] J. Nuttall and H. L. Cohen, Phys. Rev. **188**, 1542 (1969).

[11] R. Yaris and P. Winkler, J. Phys. B **11**, 1475 (1978); E. Brandas, P. Föelich, and M. Hehenberger, Int. J. Quantum Chem. **14**, 419 (1978); S. Canuto and O. Goscinski, Int. J. Quantum. Chem. **14**, 383 (1978); N. Moiseyev, P. R. Certain, and F. Weinhold, Int. J. Quantum Chem. **14**, 707 (1978).

[12] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, London, 1973).

[13] J. Simons, Annu. Rev. Phys. Chem. **28**, 15 (1977).

[14] J. Simons, J. Chem. Phys. **64**, 4541 (1976).

[15] J. D. Doll and W. P. Reinhardt, J. Chem. Phys. **57**, 1169 (1972); B. S. Yarlagadda, G. Csanak, H. S. Taylor, B. Schneider, and R. Yaris, Phys. Rev. A **7**, 146 (1973); L. S. Cederbaum, Theor. Chim. Acta **31**, 239 (1973); G. Purvis

and Y. Öhrn, J. Chem. Phys. **60**, 4063 (1974); B. T. Pickup
and O. Goscinski, Mol. Phys. **26**, 1013 (1973).

[16]The special nature of the binary product appearing in complex
coordinate calculations has been considered in detail by Wein-
hold, "Quantum Mechanics of non-Hermitian Hamiltonians,"
University of Wisconsin Reprint #WISTCI. 590.

[17]P. O. Löwdin, Phys. Rev. Sect. A **139**, 357 (1965).

[18]R. Manne, Chem. Phys. Lett. **45**, 470 (1977); E. Dalgaard,

Int. J. Quantum Chem. **15**, 169 (1979).

[19]P. D. Burrow, J. A. Michejda, and J. Conner, J. Phys. B
9, 3255 (1976).

[20]F. E. Harris and H. H. Michels, Meth. Comput. Phys. **10**,
143 (1971).

[21]C. Nehrkorn, G. D. Purvis, and Y. Öhrn, J. Chem. Phys.
64, 1752 (1976).

[22]P. Winkler, Z. Phys. A **291**, 199 (1979).