Non-Hermitian Rayleigh-Schrödinger Perturbation Theory

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We devise a non-Hermitian Rayleigh-Schrödinger perturbation theory for the single- and the multireference case to tackle both the many-body problem and the decay problem encountered, for example, in the study of electronic resonances in molecules. A complex absorbing potential (CAP) is employed to facilitate a treatment of resonance states that is similar to the well-established bound-state techniques. For the perturbative approach, the full CAP-Schrödinger Hamiltonian, in suitable representation, is partitioned according to the Epstein-Nesbet scheme. The equations we derive in the framework of the single-reference perturbation theory turn out to be identical to those obtained by a time-dependent treatment in Wigner-Weisskopf theory. The multireference perturbation theory is studied for a model problem and is shown to be an efficient and accurate method. Algorithmic aspects of the integration of the perturbation theories into existing ab initio programs are discussed, and the simplicity of their implementation is elucidated.

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I. INTRODUCTION

Electronic resonances are temporary states which decay by electron emission. Prominent examples are Auger decay [1–6], electronic decay of inner-valence ionized clusters [7–10] or temporary anions [11–16]. Electronic resonances are of fundamental importance and their study reveals deep physical insights into the complex many-body effects governing molecular physics (see, for example, Refs. [5, 6]).

Resonances cannot be described in terms of bound-state quantum mechanics because the wave functions are not part of the L²-Hilbert space, since a particle is emitted into the continuum. Hence, the wave functions are not square-integrable. Associated with each resonance is a discrete pole of the S matrix at the complex energy

$$E_{\text{res}} = E_R - i \Gamma/2.$$  \hspace{1cm} (1)

This energy is called Siegert energy [17–19]. $E_R$ is the energetic position of the resonance state and $\Gamma$ is its decay width. The Siegert wave function typically displays a localized part, near the decaying system, resembling a bound state. Asymptotically, however, the Siegert wave function diverges [19].

The discrete nature of a Siegert energy and the quasi-bound behavior of the corresponding wave function in the vicinity of the decaying system suggest to employ bound-state techniques in order to treat resonances quantitatively. This idea is exploited by a couple of methods like the stabilization method [20, 21], complex scaling [22–25], or the use of a complex absorbing potential (CAP) [26–28]. In the latter two approaches, the Siegert energy of a resonance is found as a discrete eigenvalue of a modified, non-Hermitian Schrödinger equation. The effective Siegert wave function in this eigenvalue problem is square-integrable, so that bound-state methods can indeed be applied.

Using a CAP, in particular, offers advantages when considering electronic resonances in molecules or in other extended forms of matter [28]. Its implementation in ab initio packages for bound-state quantum chemistry is simple and, in some sense, minimally invasive. For example, there is no need to modify the calculation of the Coulomb integrals. Moreover, in principle any electron-correlation method can be combined with a CAP. For example, the CAP method was implemented by Sommerfeld et al. [11] at the multireference configuration-interaction level. This program, known as CAP/CI, has already found several interesting applications (see, for instance, Refs. [12, 29]). More recently, a CAP-based extension of many-body Green’s functions was developed [30] and used to perform the first ab initio determination of resonance widths in elastic electron scattering from chlorobenzene [31].

A very promising strategy for applications to large systems is treating the CAP-Schrödinger eigenvalue problem in electronic configuration space using perturbation theory. The non-Hermitian perturbation theory derived in this article, simplifies the practical calculation of electronic resonance states considerably. We describe the combination of the method of configuration interaction with CAPs in Sec. [111] and study a non-Hermitian single-reference Rayleigh-Schrödinger ansatz in Sec. [111]. A generalization to a multireference theory is presented in Sec. [15]. In Sec. [16] the performance of the non-Hermitian multireference perturbation theory is demonstrated for a model problem. We summarize in Sec. [17].
II. COMPLEX ABSORBING POTENTIALS AND CONFIGURATION INTERACTION

In order to enable a treatment of decaying states within the framework of bound-state methods, the molecular system is enclosed by an appropriate complex potential, which enforces an absorbing boundary condition. This artificial potential, called complex absorbing potential or CAP, absorbs the emitted particle and consequently transforms the former continuum wave function into a square-integrable one \[33\]. Typically, the many-electron basis is real. Here, \( \eta \) is a real positive parameter referred to as CAP-strength parameter, and \( \hat{W} \) is called CAP operator. It is possible to choose \( \hat{W} \) as a local one-particle operator. The exact prerequisites that \( \hat{W} \) must satisfy are derived in Ref. \[27\]. A fairly general, flexible CAP for molecular calculations is presented in Refs. \[9, 29\]. (See also Sec. V, Eq. (56) for a typical \( \hat{W} \).) It should be noted that the Hamiltonian \( \hat{H}(\eta) \) in \[2\] is not Hermitian. Using the usual Hermitian inner product, it is not possible to establish an appropriate geometry in the eigenspace of \( \hat{H}(\eta) \). The natural choice is the complex symmetric bilinear form \[2, 23, 27, 28, 32\]

\[
(\varphi | \psi) := \int_{\mathbb{R}^3} \varphi(\vec{r}) \psi(\vec{r}) \, d^3r .
\]

The problem of calculating the complex Siegert energy of a resonance is equivalent to solving a complex eigenvalue equation, the CAP-Schrödinger equation \[27\]

\[
\hat{H}(\eta) | \Psi(\eta) \rangle = E(\eta) | \Psi(\eta) \rangle .
\]

If Eq. \( (4) \) is solved in a complete basis set, then there exists an eigenvalue \( E(\eta) \) such that the Siegert energy is given by \( E_{\text{res}} = \lim_{\eta \to 0} E(\eta) \). For a finite basis set, the limit \( \eta \to 0 \) merely recovers an approximation to the real spectrum of \( \hat{H} \). In this case, an optimal, finite \( \eta \) is sought, employing the condition \[3 \] \[27 \] \[28 \]

\[
| \eta \frac{dE}{d\eta} | = \text{minimum} .
\]

In a practical electron-correlation calculation, a basis

\[
\mathcal{B} = \{ | \Phi_j \rangle : \ j = 1, \ldots, K \}
\]

of square-integrable many-electron vectors \( | \Phi_j \rangle \)—often eigenvectors of an appropriate Fock operator—is introduced \[33\]. Typically, the many-electron basis is real. The matrix representation of both \( \hat{H} \) and \( \hat{W} \) is therefore real; that of \( \hat{H}(\eta) \) is complex symmetric. In other words, Eq. \( (4) \) is transformed into a complex symmetric matrix eigenvalue problem. See Ref. \[28 \] for a discussion of some of the spectral properties of complex symmetric matrices and of the numerical techniques available for diagonalizing them. Representing the Hamiltonian of a many-particle system in a systematically constructed many-particle basis set and diagonalizing the resulting matrix is known as the method of configuration interaction (CI) \[33\]. As CI matrices are in most cases huge, perturbation theory is often employed to calculate a few selected eigenstates. In the CAP/Ci problem, accelerating the calculation is even more crucial, since, according to Eq. \( (5) \), finding the Siegert energy of a resonance requires repeated diagonalization as a function of \( \eta \).

III. NON-HERMITIAN SINGLE-REFERENCE PERTURBATION THEORY

The Hamiltonian \( \hat{H} \) of the system is partitioned, following Epstein and Nesbet \[34, 35\], into an exact, diagonal part and an off-diagonal part:

\[
\hat{H} = \hat{H}_0 + \hat{H}_1
\]

\[
\hat{H}_0 = \sum_j | \Phi_j \rangle (\Phi_j | \hat{H} | \Phi_j \rangle \langle \Phi_j |
\]

\[
\hat{H}_1 = \sum_{j \neq k} | \Phi_j \rangle (\hat{H} | \Phi_k \rangle \langle \Phi_k | .
\]

The CAP operator \( \hat{W} \) is partitioned accordingly. Thus, employing \[2\], we obtain

\[
\hat{H}(\eta) = \hat{H}_0(\eta) + \hat{H}_1(\eta) ,
\]

which can be used as a starting point for a simple time-independent Rayleigh-Schrödinger perturbation theory \[37\] based on one reference \( | \Phi_1 \rangle \). Clearly, \( | \Phi_1 \rangle \) should approximate the compact bound-state-like part of the resonance wave function. In a time-dependent framework, \( | \Phi_j \rangle \) would describe the discrete, square-integrable state that undergoes decay through coupling to the continuum. We refer to \( | \Phi_1 \rangle \) as the initial state to emphasize this fact.

The CAP-Schrödinger equation for the unperturbed part of \[3\]

\[
\hat{H}_0(\eta) | \Phi_j \rangle = E_j^{(0)}(\eta) | \Phi_j \rangle ,
\]

for an arbitrary \( | \Phi_j \rangle \) \( \in \mathcal{B} \), where the unperturbed eigenenergy \( E_j^{(0)}(\eta) = (\Phi_j | \hat{H}(\eta) | \Phi_j \rangle \) is the expectation value of the full operator \( \hat{H}(\eta) \) with respect to \( | \Phi_j \rangle \). Now the well-known derivation of the Rayleigh-Schrödinger perturbation series \[37\] can be transferred to the non-Hermitian case. Up to second order, the energy of the initial state is given by

\[
E_i^{(0)}(\eta) = (\Phi_i | \hat{H}(\eta) | \Phi_i
\]

\[
E_i^{(1)}(\eta) = (\Phi_i | \hat{H}_1(\eta) | \Phi_i = 0
\]

(10a)

(10b)
\[ E^{(2)}_{i}(\eta) = \sum_{f \neq i} \frac{(\Phi_{f} \mid \hat{H}_{i}(\eta) \mid \Phi_{f})^{2}}{P_{2}(f)}. \quad (10c) \]

Note that in view of Eqs. (7) and (8), the first-order correction (10b) vanishes.

To study the real and imaginary parts of the second-order correction (10c), we assume that the matrix elements of both \( \hat{H} \) and \( \hat{W} \) are real, and we introduce an abbreviated notation:

\[
\begin{align*}
H_{jk} & := (\Phi_{j} \mid \hat{H} \mid \Phi_{k}) \\
\Delta H_{jk} & := H_{jj} - H_{kk} \\
W_{jk} & := (\Phi_{j} \mid \hat{W} \mid \Phi_{k}) \\
\Delta W_{jk} & := W_{jj} - W_{kk}.
\end{align*}
\]

In the limit \( \eta \to 0 \), the real part of \( P_{2}(f) \) reduces to

\[
\lim_{\eta \to 0} \text{Re} P_{2}(f) = \frac{H_{if}^{2}}{\Delta H_{if}}, \quad (11)
\]

which is the well-known Rayleigh-Schrödinger result for a non-degenerate state. The sum in (10c) becomes an integral in a complete basis set, and in general the principal value of this integral must be taken due to the pole on the real axis.

Now let

\[
\delta_{\epsilon}(x) = \frac{1}{\pi} \frac{\epsilon}{x^{2} + \epsilon^{2}}, \quad (12)
\]

so that Dirac’s delta function can be written as

\[
\delta(x) = \lim_{\epsilon \to 0} \delta_{\epsilon}(x). \quad (13)
\]

Equation (12) can be used to transform the imaginary part of \( P_{2}(f) \) into

\[
\text{Im} P_{2}(f) = -\pi H_{if}^{2} \delta_{\epsilon}(\Delta H_{if}) + 2 \pi \frac{H_{if} \Delta W_{if}}{\Delta H_{if}} \delta_{\epsilon}(\Delta H_{if}) + \pi \eta^{2} W_{if}^{2} \delta_{\epsilon}(\Delta H_{if}) \quad (14)
\]

with \( \epsilon := -\eta \Delta W_{if} \). The last two terms in Eq. (14) represent an artefact introduced by the CAP. However, the limit \( \eta \to 0 \) implies \( \epsilon \to 0 \), so that their contribution to \( \lim_{\eta \to 0} \text{Im} E^{(2)}_{i}(\eta) \) vanishes.

As mentioned previously, the initial state \( | \Phi_{i} \rangle \) is spatially compact. The only purpose of \( \hat{W} \) is to absorb the outgoing wave outside the molecular system. It is therefore obvious (see Refs. [9, 29]) that \( \hat{W} \) can be chosen in such a way that \( \hat{W}_{if} \) vanishes for any \( f \) (including \( f = i \)). Employing such a CAP, we find, at finite \( \eta \),

\[
\text{Im} P_{2}(f) = -\pi H_{if}^{2} \delta_{\epsilon}(\Delta H_{if}) . \quad (15)
\]

Using Eqs. (10), (11), (13), and (15), the Siegert energy, as obtained in second-order perturbation theory in the limit \( \eta \to 0 \), reads

\[
E_{\text{res}} = H_{ii} + \text{Pr} \sum_{f \neq i} \frac{H_{if}^{2}}{\Delta H_{if}} - \pi \sum_{f \neq i} H_{if}^{2} \delta(\Delta H_{if}). \quad (16)
\]

The decay width, in particular, is given by

\[
\Gamma_{i} = 2 \pi \sum_{f \neq i} H_{if}^{2} \delta(\Delta H_{if}). \quad (17)
\]

Equation (16) for \( E_{\text{res}} \) is identical to the Siegert energy derived in the framework of Wigner-Weisskopf theory [28, 37, 38], which utilizes time-dependent perturbation theory in second order in combination with the well-known relation [39]

\[
\frac{1}{x + 1 \varepsilon} = \text{Pr} \frac{1}{x} - i \pi \delta(x) . \quad (18)
\]

In a finite basis set, treating the delta function in Eq. (17) requires care. The usual approach is the direct evaluation of Eq. (17) by exploiting Stieltjes-Chebyshev moment theory [40], a cumbersome and not always numerically stable scheme. Non-Hermitian Rayleigh-Schrödinger perturbation theory offers a computationally powerful alternative: The complex energy \( E^{(2)}_{i}(\eta) \) (Eq. (10c)) is easy to calculate as a function of \( \eta \), and optimization of the complex energy in accordance with Eq. (16) immediately yields a numerical approximation to the second-order level shift in Eq. (10) and to the decay width (17).

The energies \( E^{(0)}_{i}(|\Phi\rangle) \), \( E^{(1)}_{i}(|\Phi\rangle) \), and \( E^{(2)}_{i}(|\Phi\rangle) \) in (10) are the first three terms of a perturbation series expansion of the Siegert energy associated with \( | \Phi_{i} \rangle \). Basic insight into the convergence behavior of such a series can be gained by analyzing a two-state model [41, 42]. If \( \hat{W} \) is chosen appropriately, the complex symmetric Hamiltonian matrix in a basis consisting of the compact vector \( | \Phi_{i} \rangle \) and one diffuse vector \( | \Phi_{f} \rangle \) is simply

\[
H(\eta; \lambda) = \begin{bmatrix}
H_{ii} & \lambda H_{if} \\
\lambda H_{if}^{*} & H_{ff} - i \eta W_{ff}
\end{bmatrix}, \quad (19)
\]

where \( \lambda \) controls the strength of the perturbation. The eigenvalues of this matrix are

\[
E_{\pm}(\eta; \lambda) = \frac{1}{2} (H_{ii} + H_{ff} - i \eta W_{ff}) \pm \sqrt{\frac{1}{4}(\Delta H_{if}^{2} + i \eta W_{ff})^{2} + \lambda^{2} H_{if}^{2}}.
\]

The function \( E_{\pm}(\eta; \lambda) \) has branch-point singularities, with respect to \( \lambda \), at the radius

\[
|\lambda_{BP}| = \sqrt{\frac{\Delta H_{if}^{2} + \eta^{2} W_{ff}^{2}}{2 H_{if}}}. \quad (21)
\]

The expansion of \( E_{\pm}(\eta; \lambda) \) in powers of \( \lambda \) converges at the physically relevant point \( \lambda = 1 \) if \( |\lambda_{BP}| > 1 \). In the case \( \eta = 0 \), the condition \( |\Delta H_{if}| > 2 |H_{if}| \) must therefore be satisfied. However, if decay from \( | \Phi_{i} \rangle \) into \( | \Phi_{f} \rangle \) is efficient, then we expect the energy difference, \( \Delta H_{if} \), between the two states to be small in comparison.
to the coupling strength, $H_{ij}$. A finite CAP can restore convergence under the condition that $|\eta W_{jj}| > 2|H_{ij}|$. The spectrum of the two-state matrix $H_0(\eta; \lambda = 1)$ is then nondegenerate, which ensures the existence of two linearly independent eigenvectors.\[26\]

If only a single reference is used to describe the initial state, it can happen that the optimal $\eta$ (Eq. 13) cannot compensate the quasi-degeneracy of $|\Phi_i\rangle$ with a number of pseudo-continuum states $|\Phi_f\rangle$. Another reason why the single-reference perturbation series can be divergent is strong coupling of $|\Phi_i\rangle$ to other compact states that are close in energy. Such an effect implies strong electron correlation and can cause a complete breakdown of the independent-particle picture.\[43\] Both insufficiencies can be overcome by using the multireference approach that is derived in the ensuing Sec. IV.

**IV. NON-HERMITIAN MULTIREFERENCE PERTURBATION THEORY**

The degenerate time-independent perturbation theory is a special multireference technique: A reference subspace of degenerate states, belonging to a certain unperturbed energy eigenvalue, is taken. Then the representation of the full Hamiltonian in this subspace is diagonalized to decouple the states and to yield corrections to the energy in first and to the wave function in zeroth order. If the degeneracy is removed in the new eigenvector basis, non-degenerate perturbation theory can be applied to each eigenvector to obtain higher-order corrections.\[51\]

A general multireference approach can be devised analogously. An arbitrary set of initial states can be taken. Then one can proceed as described in the previous paragraph. To carry out this program, we harness an effective Hamiltonian formalism [44–47], which has proven to be a versatile tool in many cases, see e.g. Refs. [48, 49].

**A. Effective Eigenvalue Problem**

The CAP-Schrödinger equation [4] shall be solved for several complex eigenvalues. In practice, a $K$-dimensional basis $\mathcal{B}$ (Eq. 10) is used to form a complex symmetric matrix representation of [4]. Now $n$ references are selected from $\mathcal{B}$, say, $|\Phi_j\rangle$, $j = 1, \ldots, n$ ($n \ll K$). Projection operators $[28, 29, 43, 50]$ onto the reference space and its complement space, respectively, are defined as

$$\hat{P} = \sum_{j=1}^{n} |\Phi_j\rangle\langle\Phi_j|, \quad \hat{Q} = \mathbb{1} - \hat{P} = \sum_{j=n+1}^{K} |\Phi_j\rangle\langle\Phi_j|,$$  \hspace{1cm} (22)

obeying

$$\hat{P}^2 = \hat{P}, \quad \hat{Q}^2 = \hat{Q}, \quad \hat{P}^\dagger = \hat{P}, \quad \hat{Q}^\dagger = \hat{Q}, \quad \hat{P} + \hat{Q} = \mathbb{1}, \quad \hat{P} \hat{Q} = 0.$$  \hspace{1cm} (23)

Applying [24] and [23] to [4] yields

$$E(\eta) \hat{P} |\Psi(\eta)\rangle = \hat{P} \hat{H}(\eta) \hat{P} |\Psi(\eta)\rangle$$  \hspace{1cm} (24a)$$

$$E(\eta) \hat{Q} |\Psi(\eta)\rangle = \hat{Q} \hat{H}(\eta) \hat{P} |\Psi(\eta)\rangle$$  \hspace{1cm} (24b)

Equation [24] is solved for $\hat{Q} |\Psi(\eta)\rangle$, which yields with the help of [23]

$$\hat{Q} |\Psi(\eta)\rangle = \hat{G}(\eta) \hat{Q} \hat{H}(\eta) \hat{P} |\Psi(\eta)\rangle.$$  \hspace{1cm} (25)

The operator

$$\hat{G}(\eta) := [E(\eta) \mathbb{1} - \hat{Q} \hat{H}(\eta) \hat{Q}]^{-1}$$  \hspace{1cm} (26)

is the Green’s function [33, 50] of the complement space. It has a pole where the exact eigenvalue $E(\eta)$ coincides with an eigenvalue of $\hat{Q} \hat{H}(\eta) \hat{Q}$.

Inserting Eq. [25] into [24a] results in an effective eigenvalue problem [44, 50–53]

$$\hat{H}_{\text{eff}}(\eta) \hat{P} |\Psi(\eta)\rangle = E(\eta) \hat{P} |\Psi(\eta)\rangle$$  \hspace{1cm} (27a)$$

$$\hat{H}_{\text{eff}}(\eta) = \hat{P} \hat{H}(\eta) \hat{P} + \hat{P} \hat{H}(\eta) \hat{Q} \hat{G}(\eta) \hat{Q} \hat{H}(\eta) \hat{P}$$  \hspace{1cm} (27b)

for the exact eigenvalue $E(\eta)$ associated with the eigenstate $|\Psi(\eta)\rangle$. Equation [27] is no simplification but a convenient reformulation of the original problem, Eq. [4].

Note that the matrix representation of, e.g., $\hat{P} \hat{H}(\eta) \hat{P}$ is a $K \times K$ matrix $\mathcal{PH}(\eta) \mathcal{P}$ with a nonzero $n \times n$ submatrix. For notational brevity, the $K \times K$ matrix $\mathcal{PH}(\eta) \mathcal{P}$ is identified with the smaller nonzero $n \times n$ matrix, i.e. with the representation of $\hat{P} \hat{H}(\eta) \hat{P}$ in the reference subspace.

The eigenstate $|\Psi(\eta)\rangle$ can be obtained from its projection onto the reference space, $\hat{P} |\Psi(\eta)\rangle$, by using

$$|\Psi(\eta)\rangle = \hat{P} |\Psi(\eta)\rangle + \hat{Q} |\Psi(\eta)\rangle.$$  \hspace{1cm} (28)

Inserting Eq. [25] yields

$$|\Psi(\eta)\rangle = \hat{P} |\Psi(\eta)\rangle + \hat{G}(\eta) \hat{Q} \hat{H}(\eta) \hat{P} |\Psi(\eta)\rangle.$$  \hspace{1cm} (29)

The second term in this equation represents corrections to $\hat{P} |\Psi(\eta)\rangle$ that arise from coupling to the complement space.

**B. Series Expansion**

The matrix representation of the Hamiltonian in the reference space, $\mathcal{PH}(\eta) \mathcal{P}$, can be diagonalized to decouple the reference configurations. To this end, the complex symmetric eigenvalue problem

$$\mathcal{PH}(\eta) \mathcal{P} |\Psi(\eta)\rangle = Q(\eta) E^{(0)}(\eta)$$  \hspace{1cm} (30)

$$E^{(0)}(\eta) = \text{diag}(E^{(0)}_1(\eta), \ldots, E^{(0)}_n(\eta))$$
has to be solved. If $\mathbf{P H}(\eta)\mathbf{P}$ is diagonalizable \[\ref{eq:42}, \ref{eq:43}\], then $Q(\eta)Q(\eta)^T = Q(\eta)^TQ(\eta) = \mathbf{1}$. In this case, $Q(\eta)$ allows us to perform a transformation from $B = \{|\Phi_j\rangle : j = 1, \ldots, K\}$ to a more useful orthonormal basis:

$$|\varphi_j(\eta)\rangle = \left\{ \sum_{k=1}^{n} Q_{kj}(\eta) |\Phi_k\rangle \quad ; j \in \{1, \ldots, n\} \right\} \ {}\ {}|\Phi_j\rangle \quad ; j \in \{n + 1, \ldots, K\} .$$

Let

$$\hat{H}_{jk}(\eta) := (\varphi_j(\eta)|\hat{H}(\eta)|\varphi_k(\eta))$$

denote the matrix elements of $\hat{H}(\eta)$ with respect to the new basis \[\ref{eq:31}\]. We observe that

$$\hat{H}_{jk}(\eta) = E_j^{(0)}(\eta) \delta_{jk} , \quad j, k = 1, \ldots, n ,$$

and apply to the full matrix $\hat{H}(\eta)$ Epstein-Nesbet partitioning \[\ref{eq:32}, \ref{eq:33}\] into diagonal and off-diagonal parts:

$$\hat{H}(\eta) = H_0(\eta) + \lambda H_1(\eta) .$$

The parameter $\lambda$ is introduced, as in Eq. \[\ref{eq:19}\], to allow for a systematic perturbation expansion (Sec. IV C). Employing Eq. \[\ref{eq:34}\], the effective Hamiltonian, Eq. \[\ref{eq:27}\], represented in the new basis, Eq. \[\ref{eq:31}\], reads

$$H_{\text{eff}}(\eta) = E^{(0)}(\eta) + \lambda^2 Q(\eta)^T \mathbf{P} \mathbf{H}(\eta) Q \times G(\eta) \mathbf{Q} H(\eta) \mathbf{P} Q(\eta) .$$

With the definition

$$\Psi_k(\eta) := (\varphi_k(\eta)|\Psi(\eta)), \quad k = 1, \ldots, K ,$$

the complex eigenvalue problem of $H_{\text{eff}}(\eta)$ can be written as

$$\sum_{l=1}^{n} (H_{\text{eff}}(\eta))_{kl} \Psi_l(\eta) = \lambda E(\eta) \Psi_k(\eta), \quad k = 1, \ldots, n . \tag{37}$$

In order to solve Eqs. \[\ref{eq:35} \] and \[\ref{eq:37}\], the matrix $G(\eta)$ of the Green’s function $\hat{G}(\eta)$, Eq. \[\ref{eq:20}\], must be evaluated. We set $H_{\text{eff}}^{\text{QQ}}(\eta) := (\mathbf{Q} \hat{H}(\eta) \mathbf{Q})_{\text{diagonal}}$ and $H_{\text{eff}}^{\text{QQ}}(\eta) := (\mathbf{Q} \hat{H}(\eta) \mathbf{Q})_{\text{off-diagonal}}$, so that

$$G(\eta) = [E(\eta) \mathbf{1} - H_{\text{eff}}^{\text{QQ}}(\eta) - \lambda H_{\text{eff}}^{\text{QQ}}(\eta)]^{-1} . \tag{38}$$

The eigenvector $(\Psi_1(\eta), \ldots, \Psi_K(\eta))$ of $\hat{H}(\eta)$ converges, in the limit $\lambda \to 0$, to a Cartesian unit vector $\hat{e}_j \in \mathbb{C}^K$ for some fixed $j$:

$$\lim_{\lambda \to 0} \Psi_k(\eta) = \delta_{jk} . \tag{39}$$

Let us assume the reference space is chosen such that $j \in \{1, \ldots, n\}$. Then,

$$\lim_{\lambda \to 0} E(\eta) = E_j^{(0)}(\eta) . \tag{40}$$

Provided that

$$\| \mathcal{g}(\eta) \{ (E^{(0)}(\eta) - E_j^{(0)}(\eta)) \mathbf{1} - \lambda H_{\text{eff}}^{\text{QQ}}(\eta) \} \| < 1 \tag{41}$$

holds, where

$$\mathcal{g}(\eta) := [E_j^{(0)}(\eta) \mathbf{1} - H_{\text{eff}}^{\text{QQ}}(\eta)]^{-1} , \tag{42}$$

$G(\eta)$ in Eq. \[\ref{eq:38}\] can be expanded in a geometric series (according to Lemma 2.3.3 in Ref. \[\ref{eq:54}\], which also holds for complex matrices): \[\ref{eq:43}\]

$$G(\eta) = \left[ \sum_{k=0}^{\infty} (-1)^k \left( \mathcal{g}(\eta) \{ (E^{(0)}(\eta) - E_j^{(0)}(\eta)) \mathbf{1} - \lambda H_{\text{eff}}^{\text{QQ}}(\eta) \} \right)^k \right] \mathcal{g}(\eta) . \tag{43}$$

Condition \[\ref{eq:41}\] is, of course, satisfied in the limit $\lambda \to 0$, in view of Eq. \[\ref{eq:40}\]. At $\lambda = 1$, \[\ref{eq:41}\] implies that the series \[\ref{eq:43}\] converges only if the unperturbed energy $E_j^{(0)}(\eta)$ is well separated from all diagonal elements of $\mathbf{Q} \hat{H}(\eta) \mathbf{Q}$. This can, in principle, always be enforced by choosing a sufficiently large number of references.

### C. Approximation

The matrix $G(\eta)$ in Eq. \[\ref{eq:43}\] still depends on the exact energy $E(\eta)$. Equations \[\ref{eq:35}, \ref{eq:37}\], \[\ref{eq:39}\] allow us to make the following perturbative ansatz:

$$E(\eta) = E_j^{(0)}(\eta) + \sum_{i=2}^{4} \lambda^i E^{(i)}(\eta) + O(\lambda^5) . \tag{44}$$

Thus, an expansion of the Green’s function in terms of $\lambda$,

$$G(\eta) = \sum_{i=0}^{2} \lambda^i G^{(i)}(\eta) + O(\lambda^3), \tag{45}$$

can be determined:

$$G^{(0)}(\eta) = \mathcal{g}(\eta)$$
$$G^{(1)}(\eta) = \mathcal{g}(\eta) H_{\text{eff}}^{\text{QQ}}(\eta) \mathcal{g}(\eta)$$

$$G^{(2)}(\eta) = \mathcal{g}(\eta) \{ (E^{(0)}(\eta) - E_j^{(0)}(\eta)) \mathbf{1} - \lambda H_{\text{eff}}^{\text{QQ}}(\eta) \} \mathcal{g}(\eta)$$
\[ G^{(2)}(\eta) = g(\eta) H_1^{Q_Q}(\eta) g(\eta) H_1^{Q_Q}(\eta) g(\eta) - E^{(2)}(\eta) g(\eta)^2. \]  

Utilizing Eqs. (35) and (40), a perturbation series for the effective Hamiltonian is obtained, which is inserted into the effective eigenvalue problem (37), together with the expansion (see Eq. (39))

\[ \Psi_k(\eta) = \delta_{jk} + \sum_{i=1}^{2} \lambda^i \Psi_k^{(i)}(\eta) + O(\lambda^3). \]  

Chen et al. have independently derived a formally similar theory in Ref. [4], using a direct Taylor series expansion of the secular equation for the energy of bound states of a molecular system. They provide explicit expressions for the perturbation expansion of the real energy up to third order. Chen et al. further observe that this kind of multireference approach reduces to single-reference Epstein-Nesbet perturbation theory if only one reference is used. Of course, the non-Hermitian multireference perturbation theory of this section also reduces to the non-Hermitian single-reference theory.

From the perturbative treatment of Eq. (37) we further conclude, for \( k = 1, \ldots, n \) \( (k \neq j) \), that

\[ \Psi_j^{(1)}(\eta) = 0 \]  

for all \( i \geq 1 \). Upon sorting for orders in \( \lambda \), the energy corrections, up to fourth order, are found to be

\[ E^{(2)}(\eta) = \sum_{k=n+1}^{K} \frac{\hat{H}_{jk}(\eta)^2}{E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta)} \]  

(49a)

\[ E^{(3)}(\eta) = \sum_{k,l=n+1}^{K} \frac{\hat{H}_{jk}(\eta) \hat{H}_{kl}(\eta) \hat{H}_{lj}(\eta)}{(E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta))(E_j^{(0)}(\eta) - \hat{H}_{ll}(\eta))} \]  

(49b)

\[ E^{(4)}(\eta) = \sum_{k,l=n+1}^{K} \sum_{l',l''=1}^{n} \frac{\hat{H}_{kl}(\eta)^2 \hat{H}_{lj}(\eta)^2}{(E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta))^2 (E_j^{(0)}(\eta) - \hat{H}_{ll}(\eta))^2} \]  

(49c)

\[ - E^{(2)}(\eta) \sum_{k=n+1}^{K} \frac{\hat{H}_{jk}(\eta)^2}{(E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta))^2} \]  

\[ + \sum_{k,l,n+1}^{K} \frac{\hat{H}_{jk}(\eta)^2 \hat{H}_{kl}(\eta)^2}{(E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta))^2 (E_j^{(0)}(\eta) - \hat{H}_{ll}(\eta))}. \]

These results represent corrections to the wave function in the reference space. Corrections to the eigenvector that affect only components with respect to the complement space can be obtained from (49). Hence, the components \( \Psi_k(\eta), k = n + 1, \ldots, K \), are given by

\[ \Psi_k(\eta) = \lambda \sum_{l=1}^{n} (G(\eta) Q H(\eta) P Q(\eta))_{kl} \Psi_l(\eta). \]  

(51)

Using Eqs. (45), (46), (47), (48), and (50), the first- and second-order corrections of the eigenvector in the complement space are as follows \( (k = n + 1, \ldots, K) \):
\begin{align}
\Psi_k^{(1)}(\eta) &= \frac{\hat{H}_{kj}(\eta)}{E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta)}, \\
\Psi_k^{(2)}(\eta) &= \sum_{i=n+1}^{K} \frac{\hat{H}_{ki}(\eta) \hat{H}_{ij}(\eta)}{(E_j^{(0)}(\eta) - \hat{H}_{kk}(\eta)) (E_j^{(0)}(\eta) - \hat{H}_{ii}(\eta))}.
\end{align}

These corrections to the wave function can also be useful for the real case ($\eta = 0$) since they are not explicitly given in Ref. [34].

\section{D. Computational Algorithm}

In iterative eigenvalue solvers, as for example the Lanczos \cite{54,56} or the Davidson \cite{57} algorithm, a matrix-vector multiplication is carried out in each iteration. This is the slowest step in these algorithms, and it therefore determines their overall performance. The following sketch of an algorithm for the fourth-order treatment of the Siegert energy, Eq. (49), reveals that this perturbative approach is roughly as expensive as a single iteration of an iterative block-eigenvalue solver.

1. Choose a set of $n$ references. Perform a full diagonalization of the complex symmetric matrix representation of $\hat{H}(\eta)$ in the reference space ($H_{kl}(\eta)$, $k, l = 1, \ldots, n$) to obtain $E_j^{(0)}(\eta)$ and $Q(\eta)$. A highly efficient program for this purpose is described in Ref. [58].

2. Determine all many-particle configurations, beyond the reference space, that contribute to the energy in (49). Since, for electronic-structure problems, $\hat{H}(\eta)$ consists of one- and two-body operators, a consistent treatment in fourth order requires the inclusion of single, double, triple, and quadruple excitations of the references. These excitations form the complement space and define, together with the references, the total vector space dimension, $K$. Calculate and store all diagonal matrix elements of $\hat{H}(\eta)$ with respect to the complement space: $d_k(\eta) := H_{kk}(\eta)$, $k = n + 1, \ldots, K$.

3. Let $E_j^{(2)}(\eta) = E_j^{(4,1)}(\eta) = E_j^{(4,2)}(\eta) = 0$, $j = 1, \ldots, n$. Loop over $k$ ($k = n + 1, \ldots, K$):

   (a) Transform column $k$ of the coupling block:

   \[ \hat{H}_{jk}(\eta) = \sum_{l=1}^{n} Q_{lj}(\eta) H_{lk}(\eta), \quad j = 1, \ldots, n \]

   (b) For $j = 1, \ldots, n$ do

   \[ E_j^{(2)}(\eta) = E_j^{(2)}(\eta) + \frac{\hat{H}_{jk}(\eta)^2}{E_j^{(0)}(\eta) - d_k(\eta)} \]

4. Let $E_j^{(3)}(\eta) = E_j^{(4,3)}(\eta) = 0$, $j = 1, \ldots, n$. Loop over $k$ from $n + 1$ to $K$, for each $j \in \{1, \ldots, n\}$:

   (a) $S_k(\eta) = \sum_{l=n+1}^{K} \frac{\hat{H}_{jl}(\eta) H_{lk}(\eta) (1 - \delta_{kl})}{E_j^{(0)}(\eta) - d_l(\eta)}$

   (b) $T_k(\eta) = \sum_{l=n+1}^{K} \left( \frac{\hat{H}_{jl}(\eta) H_{lk}(\eta) (1 - \delta_{kl})}{E_j^{(0)}(\eta) - d_l(\eta)} \right)^2$

5. $E_j^{(4,3)}(\eta) = E_j^{(4,3)}(\eta) + \frac{\hat{H}_{jk}(\eta) S_k(\eta)}{E_j^{(0)}(\eta) - d_k(\eta)}$

The algorithm requires that at least two vectors of the dimension of the complement space can be held in memory. If more memory is available (core memory or hard disk), at least some of the transformed matrix elements $\hat{H}_{jk}(\eta)$ should also be kept. Otherwise, all of them have to be recalculated in step 4. The matrix $H_{kl}(\eta)$, $k, l = n + 1, \ldots, K$, in the complement space is in general
much too big to be stored (except for the diagonal elements $d_k(\eta)$), so that recalculation is the only practical option.

For a second-order treatment, the algorithm simplifies considerably. Only steps 1, 2, 3(a), and the step affecting $E^{(2)}(\eta)$ in 3(b) are needed. The memory requirements are minimal. The second-order perturbation theory can thus be applied to large systems not amenable to a solution by an iterative diagonalization procedure.

Note that in second order only single and double excitations of the reference configurations play a role. This is also true in third order. In third order, however, in addition 3(c) and the first halves of 4(a) and 4(b) have to be carried out. Step 4(a) implies the multiplication of the Hamiltonian matrix in the complement space with a vector (for each $j$). This increases the computational effort significantly and is comparable to a single step in an iterative block diagonalization procedure. As mentioned previously, in the fourth-order formalism, triple and quadruple excitations add a new level of complexity.

Recall that the CAP strength $\eta$ must be optimized in order to fulfill Eq. (5) for those resonances that can be approximated well within the reference space. The second-order approach is exceptionally simple. It should therefore be employed to identify potential resonances and to preoptimize $\eta$ for each of them. Then, the expensive step 4 can be restricted to a few selected $j \in \{1, \ldots, n\}$ and to a relatively small $\eta$ range. In this way, the inclusion of higher-order corrections to the Siegert energies can be achieved particularly efficiently.

V. MODEL PROBLEM

A model problem is studied in this section, which serves to illustrate the multireference perturbation theory derived in Sec. III. We consider $s$-wave scattering of an electron from the spherically symmetric potential $28$

$$V(r) = \begin{cases} -V_0 & ; 0 \leq r < a \\ V_0 & ; a \leq r < 2a \\ 0 & ; r \geq 2a \end{cases} .$$

The effective one-dimensional Hamiltonian for this problem reads, in atomic units,

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dr^2} + V(r) .$$

There exists a quasi-analytic solution $28$, giving $-6.353803650$ for the only bound state and

$$E_{1st} = 4.001414397 - 0.003616371 i$$

for the first resonance, assuming $V_0 = 10$, $a = 1$.

In the following we employ the CAP operator

$$\hat{W} = \begin{cases} (r - c)^2 & ; r \geq c \\ 0 & ; 0 \leq r < c \end{cases} .$$

The parameter $c$ defines a sphere about the origin, inside of which the CAP does not affect the wave function. If $c$ is too large, with respect to a chosen finite basis set, then an outgoing wave will be reflected by the basis set wall and will not be absorbed by the CAP. Conversely, if $c$ is too small, the perturbation of the wave function near the origin is too large. A good choice is $c = 2a = 2$. $28$

The CAP Hamiltonian $\hat{H}(\eta)$ of the model problem is given by Eqs. \(28\), \(126\), and \(130\). The matrix representation of $\hat{H}(\eta)$ is constructed using a basis of particle-in-a-box functions ($k = 1, \ldots, K$)

$$\phi_k(r) = \begin{cases} \sqrt{\frac{2}{L}} \sin \left( \frac{k\pi r}{L} \right) & ; 0 \leq r < L \\ 0 & ; r \geq L \end{cases} .$$

A spatial extension of the basis set of $L = 10$ is assumed throughout, which is sufficiently large compared with $c = 2$. Furthermore, a basis dimension of $K = 5000$ is chosen.

A particle-in-a-box function is not a good reference, because its overall shape differs substantially from that of a resonance wave function $28$. Hence, the overlap between the best references and the resonance itself is small. The matrix representation in the basis \(67\) therefore has little similarity with a CI matrix. An improved matrix representation of the real Hamiltonian \(54\) can be created by diagonalizing the matrix representation of \(54\) in a basis of particle-in-a-box functions \(67\) for a potential well depth of $V_0 = 20$. The $n$ energetically lowest eigenvectors in this modified potential serve as references. The matrices of the real and imaginary parts for $V_0 = 10$ are then formed with the help of \(67\) and projected onto the real eigenbasis calculated with $V_0 = 20$. This procedure yields matrices that are nearly diagonally dominant, and thus they bear more resemblance to CI matrices. Especially the near diagonal dominance of the matrix representation assures a sufficient overlap of the best references with the first resonance of the model problem. Nevertheless, single-reference perturbation theory is not adequate for this example.

In order to demonstrate the usefulness of multireference perturbation theory in the non-Hermitian case, we compute the Siegert energy of the first resonance in two ways. First, we diagonalize $\hat{H}(\eta)$ in the reference space and employ Eq. (59) without any perturbative correction. It turns out that in this case more than 20 references are needed to satisfy the optimization criterion (55). Second, we apply the second-order scheme, Eq. (19a). The results are compared in Fig. 1 as a function of the number of references, $n$. The real and imaginary parts of the computed Siegert energy are shown separately. The dotted horizontal lines in the figure indicate the exact values (55). It is evident that the convergence of the Siegert energy with increasing $n$ can be accelerated considerably by the application of perturbation theory. Not only is it possible, in the second-order approach, to satisfy Eq. (59) with a relatively small number of references, the accuracy at a given $n$ is also significantly improved.

In this example, the application of multireference per-
FIG. 1. (Color online) The complex Siegert energy of the energetically lowest resonance in the model potential, Eq. (53), for an increasing number of references. The resonance energy is computed (a) by solving the CAP-Schrödinger eigenvalue problem just within the reference space (squares in the figure) and (b) by non-Hermitian multireference perturbation theory up to second order (circles). The real part of the Siegert energy is shown in the upper panel, the imaginary part in the lower one. The dotted horizontal lines indicate the exact values [55].

VI. CONCLUSION

Non-Hermitian Rayleigh-Schrödinger perturbation theories, based on Epstein-Nesbet partitioning, have been devised and examined in this article. The single-reference perturbation theory takes about 80 s for 40 references and 70 steps with varying $\eta$. Carrying out a full diagonalization for 70 different $\eta$ values takes approximately 20 d on the same computer.

and the multireference theory are interesting tools for investigating the decay properties of resonance states—which represent the most conspicuous manifestation of quantum effects in scattering processes. Use of a complex absorbing potential is made in order to transform the time-dependent decay problem into a non-Hermitian, time-independent, bound-state-like problem that can be treated with $L^2$ techniques.

In a complete basis set, the single-reference perturbation theory turns out to lead to equations identical to those obtained in the framework of Wigner-Weisskopf theory. However, the non-Hermitian theory offers computational advantages that should be exploited.

Flexibility can be added by using more than one reference. We have developed the non-Hermitian multireference perturbation theory through fourth order with respect to the energy and through second order for the wave function. The application to a model problem illustrates the efficiency and accuracy of the method.

The integration of non-Hermitian perturbation theory into existing ab initio programs for solving the electronic-structure problem in finite systems is straightforward and is presently carried out utilizing the multireference configuration-interaction program DIESEL [59–61]. The matrix elements of the CAP operator can be obtained efficiently [29], with only minor modification of the DIESEL program. The second-order non-Hermitian multireference perturbation theory, in particular, may open the door to a theoretical understanding of electronic resonance physics in large molecular systems.

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