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Reference-state one-particle density-matrix theory

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A density-matrix formalism is developed based on the one-particle density-matrix of a single-determinantal reference state. Unlike traditional density-functional-theory approaches, the v-representable problem does *not* appear in the proposed method, nor the need to introduce functionals defined by a constrained search. The correlation-energy functionals are nonuniversal, in the sense that they depend on the external potential. Nevertheless, model systems can still be used to derive universal energy functionals. Variational and nonvariational energy functionals are introduced that yield the target-state energy when the reference state—or its corresponding one-particle density matrix—is constructed from Brueckner orbitals. Nonvariational energy functionals yield generalized Hartree-Fock equations involving a nonlocal correlation potential and the Hartree-Fock exchange operator; these equations are obtained by imposing the Brillouin-Brueckner condition. The same equations—for the most part—are obtained from variational energy functionals using functional minimization, yielding the (kernel of the) correlation potential as the functional derivative of correlation-energy functionals. Approximations for the correlation-energy functions are introduced, including a one-particle-density-matrix variant of the local-density approximation, a variant of the Colle-Salvetti functional, and a linear combination of the two that is a variant of the correlation-energy functional within the hybrid, three-parameter, Becke-Lee-Yang-Parr density functional (B3LYP).

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I. INTRODUCTION

Many variants of density-functional theory (DFT) [1–6] share common features with the Hartree-Fock approach. In particular, the Kohn-Sham method [7] uses orbital equations that appear similar, in certain respects, with the ones from Hartree-Fock theory. On the other hand, unlike the Hartree-Fock wave function, the Kohn-Sham determinantal state shares only a common density with the exact wave function, and is *not* considered an approximation of the ground state. Furthermore, in contrast to the exchange potential from Hartree-Fock theory, the Kohn-Sham exchange-correlation potential is a local operator.

DFT approaches that use hybrid functionals [8–11] introduce a component of exact exchange energy, where justification, in part, for this modification comes from the adiabatic connection [12–16], yielding an approach that, again, has more similarities with Hartree-Fock, especially since the exchange component yields a nonlocal potential—the Hartree-Fock exchange—that depends on the one-particle density matrix of the Kohn-Sham determinantal state. The most celebrated hybrid functional, the three-parameter, Becke-Lee-Yang-Parr density functional (B3LYP) [8,17], contains two correlation-energy functionals, the Dirac-exchange functional with a correction, and, of course, exact exchange. The LYP (Lee, Yang, and Parr) density functional [18]—a key component of B3LYP—is derived from the Colle-Salvetti correlation-energy functional [19], where this functional depends on a one-particle density matrix, say $\tilde{\gamma}$, and $\tilde{\gamma}$ is from the *Hartree-Fock* reference state—and not from an *exact* eigenstate—indicating a further evolutionary step of DFT methods towards a Hartree-Fock generalization with inclusion of electron correlation.

In the Hartree-Fock Kohn-Sham approach [20], the exchange energy is treated in an exact manner and the nonlocal, Hartree-Fock exchange potential appears in the orbital equations. A generalization of this approach by Lindgren and Salomonson [21] yields, in addition, a nonlocal correlation potential and orbitals that, they believe, are very similar to Brueckner orbitals. Other workers also suggest that Brueckner and Kohn-Sham orbitals are very similar [22].

Brueckner orbital theory [21,23–37] is a generalization of Hartree-Fock theory that utilizes a single-determinantal state that has the maximum overlap with an exact eigenfunction [38,39]. Below we use this formalism to develop a density-matrix theory, in which a variety of variational and nonvariational energy functionals are introduced that depend on the one-particle density matrix, say γ. Unlike other approaches, where γ is the one-particle density matrix of an exact eigenfunction [40–45], the introduced method—called *reference-state one-particle density-matrix theory*—has γ arising from a single-determinantal reference state, where the energy functionals yield the exact energy when γ is the one from the Brueckner reference state.

Below, generalized Hartree-Fock equations are obtained containing the exact exchange potential and a nonlocal correlation potential, where these equations are obtained using the Brillouin-Brueckner condition, from nonvariational energy functionals, and functional minimization, from variational functionals. Both variational and nonvariational approaches lead to the same correlation potential and generalized Fock operator. (The correlation potentials and

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generalized Fock operator from either approach are the same, in the sense that the Brueckner orbitals obtained from the *variational* approach can differ only from the orbitals obtained from the *nonvariational* approach by a unitary transformation.)

One advantage that this density-matrix approach has over traditional density-functional formalisms—or other one-particle density-matrix formalisms—is that there is no v-representable problem [1,2,46] nor the need to introduce functionals defined by a constrained search [43,47,48]. Furthermore, the necessary conditions for a one-particle density matrix γ to come from a single determinant are known, so they can be expressed as constraints when minimizing variational-energy functionals that depend on γ [49,50].

In contrast to Kohn-Sham DFT, the correlation-energy functionals introduced below depend on the external potential, and are, therefore, in this sense, nonuniversal functionals. Nevertheless, approximate functionals can still be derived from model systems. For example, as discussed below, the electron-gas correlation energy can be used in an *electron-gas approximation*, where, unlike the local-density approximation (LDA) [7], the gas is not required to be uniform; furthermore, the Colle-Salvetti functional [19]—derived from the helium atom—is also a reasonable approximation within the proposed method, even though it is a universal functional.

Section II presents a short review of perturbation and coupled cluster theory that emphasizes the dependence, of the operators from these methods, on the determinantal reference state. Four trial wave functions are introduced in Sec. IV that generate the exact, or target state of interest, when the Brillouin-Brueckner condition—reviewed in Sec. III—is satisfied, or, equivalently, when the reference states for the trial wave functions are constructed from Brueckner orbitals. Also in Sec. IV, nonvariational correlation-energy functionals are introduced that depend on the reference state, and these functionals generate the exact correlation energy when the reference state is the one constructed from Brueckner orbitals. Using the trial wave functions, a nonvariational Brueckner-orbital formalism is presented in Sec. V, yielding generalized, or exact, Fock operators, permitting the determination of the Brueckner reference state that can be used to obtain the exact correlation energy from the correlation-energy functionals.

Because of the one-to-one correspondence between the set of determinant states and their one-particle density matrices, the correlation-energy functionals—or any functionals that depend on the reference state—can be written as functionals of the one-particle density matrix, as indicated in Sec. VI. A variational formalism is presented in Sec. VIII, permitting correlation potentials to be determined from the functional derivative of correlation-energy functionals. Approximations for the correlation-energy functions are introduced in Secs. VII and VIII.

Elsewhere [51], using time-independent many-body perturbation theory [52–54], diagrammatic expansions are given for the nonvariational energy functionals that are expressed in terms of orbitals and orbital energies. When severe restrictions are placed on the orbital energies, the individual diagrams are shown to *explicitly* depend on the one-particle density matrix of the reference state. (The diagrammatic expansions for the variational-energy functionals can also be generated [55].) In addition, the correlation-energy functionals can be partitioned into individual terms that are—to a varying degree—universal, yielding another approach to derive approximate functionals from model systems [51].

II. PERTURBATION AND COUPLED CLUSTER THEORY

A. The exact and correlation energies

We seek a solution of the time-independent Schrödinger equation,

$$H|\Psi\rangle = \mathcal{E}|\Psi\rangle, \tag{1}$$

where $|\Psi\rangle$ is an eigenstate of the Hamiltonian operator,

$$H = \sum_{ij} [i|\hat{h}|j] a_i^\dagger a_j + \frac{1}{2}\sum_{ijkl} [ij|kl] a_i^\dagger a_k^\dagger a_l a_j, \tag{2}$$

and the integrals are written using chemist's notation [56]:

$$[i|\hat{h}|j] = \left[i \left| \left(-\frac{1}{2}\nabla^2 \right) \right| j \right] + [i|v|j], \tag{3}$$

$$[ij|kl] = \sum_{\omega_2\omega_2} \int \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) r_{12}^{-1} \psi_k^*(\mathbf{x}_2)\psi_l(\mathbf{x}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{4}$$

where the spatial and spin coordinates, $\mathbf{r}$ and ω, are denoted collectively by $\mathbf{x}$.

The wave function of interest $|\Psi\rangle$, or target state, can be generated by a wave operator Ω_Φ:

$$\Omega_\Phi|\Phi\rangle = |\Psi\rangle, \tag{5}$$

where $|\Phi\rangle$ is any determinantal state that overlaps with the target state: $\langle\Phi|\Psi\rangle \neq 0$.

The reference state $|\Phi\rangle$ is completely defined by its occupied orbitals; we denote these orbitals by $\{\psi_o \rightarrow \Phi\}$; the set of unoccupied orbitals—the virtual orbital set—is denoted by $\{\psi_u \rightarrow \Phi\}$. The virtual set $\{\psi_u \rightarrow \Phi\}$ also determines the occupied set, since the two sets are orthogonal, and the union of the two sets is a complete set. Hence, $\{\psi_u \rightarrow \Phi\}$ also determines $|\Phi\rangle$. Unless stated otherwise, two sets of either occupied or unoccupied orbitals that differ by a unitary transformation are considered equivalent.

We use the following orbital convention: Arbitrary orbitals are denoted by i and j; occupied orbitals are denoted by w, x, and y; virtual orbitals are denoted by r, s, and t:

$$\psi_w, \psi_x, \psi_y \in \{\psi_o \rightarrow \Phi\}, \tag{6a}$$

$$\psi_r, \psi_s, \psi_t \in \{\psi_u \rightarrow \Phi\}, \tag{6b}$$

$$\psi_i, \psi_j, \psi_k \in \{\psi_o \rightarrow \Phi\} \cup \{\psi_u \rightarrow \Phi\}. \tag{6c}$$

Explicitly, our spin orbitals $\psi_i(\mathbf{x})$ have the following form:

$$\psi_i(\mathbf{x}) = \chi_{i\sigma}(\mathbf{r})\sigma(\omega), \quad \sigma = \alpha \text{ or } \beta, \tag{7}$$

where the spin and spatial portions are given by $\sigma(\omega)$ and $\chi_{i\sigma}(\mathbf{r})$, respectively, and the spatial functions $\chi_{i\sigma}(\mathbf{r})$ are permitted to be unrestricted—two spin orbitals do not, in general, share the same spatial function.

By multiplying the Schrödinger equation (1) from the left by $\langle\Phi|$, and requiring intermediate normalization to be satisfied,

$$\langle\Phi|\Psi\rangle = \langle\Phi|\Omega_\Phi|\Phi\rangle = 1, \tag{8}$$

we get

$$\mathcal{E} = \langle\Phi|H|\Psi\rangle = E_1[\Phi] + \mathcal{E}_{co}[\Phi], \tag{9}$$

where the first-order energy is

$$E_1[\Phi] = \langle\Phi|H|\Phi\rangle = \sum_{w\in\{\psi_o\to\Phi\}} \left[w \left| \left(-\frac{1}{2}\nabla^2 + v + \tfrac{1}{2}(J_\Phi - K_\Phi) \right) \right| w \right], \tag{10}$$

and the Coulomb $J_\Phi(\mathbf{r})$ and exchange $K_\Phi(\mathbf{x})$ operators have their usual forms

$$[i|J_\Phi|j] = \sum_{x\in\{\psi_o\to\Phi\}} [xx|ij], \tag{11}$$

$$[i|K_\Phi|j] = \sum_{x\in\{\psi_o\to\Phi\}} [xi|jx]; \tag{12}$$

furthermore, the correlation energy $\mathcal{E}_{co}[\Phi]$, given by

$$\mathcal{E}_{co}[\Phi] = \langle\Phi|H|\Psi_{Q_\Phi}\rangle, \tag{13}$$

is obtained from the correlation function:

$$|\Psi_{Q_\Phi}\rangle = Q_\Phi|\Psi\rangle, \tag{14}$$

where the orthogonal-space projector satisfies

$$1 = Q_\Phi + P_\Phi, \tag{15}$$

and the reference-space projector is given by

$$P_\Phi = |\Phi\rangle\langle\Phi|. \tag{16}$$

The first-order energy can also be written as

$$E_1[\Phi] = \langle\Phi|H|\Phi\rangle = (H)_{\rm cl}, \tag{17}$$

where the cl subscript indicates the closed portion—the fully contracted terms that, diagrammatically speaking, have no external free lines [53,54,57,58]. Appendix A presents partitioning of second-quantized operators into *closed* and *open* portions in a slightly different manner than is done by other authors.

Similar to the first-order energy, for the correlation energy we have

$$\mathcal{E}_{\rm co}[\Phi] = (H\chi_\Phi)_{\rm cl}, \tag{18}$$

where the correlation operator χ_Φ, defined by

$$\Omega_\Phi = 1 + \chi_\Phi, \tag{19}$$

generates the correlation function $|\Psi_{Q_\Phi}\rangle$ when operating on the reference state:

$$\chi_\Phi|\Phi\rangle = |\Psi_{Q_\Phi}\rangle. \tag{20}$$

As indicted by Eq. (9), the sum of Eqs. (17) and (18) gives the exact energy

$$\mathcal{E} = (H\Omega_\Phi)_{\rm cl}. \tag{21}$$

Let us also write down the expression for the exchange-correlation (XC) energy

$$\mathcal{E}_{xc}[\Phi] = \mathcal{E}_{co}[\Phi] - E_x[\Phi], \tag{22}$$

where the exchange energy $E_x[\Phi]$ is the last term on the right side of Eq. (12):

$$E_x[\Phi] = \frac{1}{2}\sum_{w\in\{\psi_o\to\Phi\}} [w|K_\Phi|w]. \tag{23}$$

B. The linked cluster theorem

The wave operator Ω_Φ can be expressed in an exponential form [54,57–64],

$$\Omega_\Phi = e^{S_\Phi} = 1 + S_\Phi + \frac{1}{2!}S_\Phi^2 + \frac{1}{3!}S_\Phi^3 + \cdots, \tag{24a}$$

where the cluster operator S_Φ can be written as a sum of one-, two-, and higher-body terms,

$$S_\Phi = S_1^\Phi + S_2^\Phi + S_3^\Phi + \cdots, \tag{24b}$$

and these amplitudes are defined by the following relations:

$$S_1^\Phi = \sum_{rw} s_{rw}^\Phi a_r^\dagger a_w, \tag{25a}$$

$$S_2^\Phi = \frac{1}{2!}\sum_{rwsx} s_{rwsx}^\Phi a_r^\dagger a_s^\dagger a_x a_w, \tag{25b}$$

$$S_3^\Phi = \frac{1}{3!}\sum_{rwsxty} s_{rwsxty}^\Phi a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w, \tag{25c}$$

$$\vdots$$

which use the orbital convention given by Eqs. (6). The cluster operator S_Φ and its amplitudes S_n^Φ are invariant to a unitary transformation of the occupied or virtual orbitals [30].

Since S_Φ—given by Eq. (24b)—is open, only connected (cn) portions contribute to the correlation and exact energies, $\mathcal{E}_{\rm co}[\Phi]$ and $\mathcal{E}$, given by Eqs. (18) and (21). Therefore, we can write

$$\mathcal{E}_{\rm co}[\Phi] = (H\chi_\Phi)_{\rm cl,cn}, \tag{26}$$

$$\mathcal{E} = (H\Omega_\Phi)_{\rm cl,cn}, \tag{27}$$

where the additional cn subscripts indicate that only the connected portions contribute—contractions in which all S_Φ amplitudes are connected together by H.

Equation (27) indicates that the closed part of $(H\Omega_\Phi)_{\rm cn}$ gives the energy of interest, $\mathcal{E}$; the vanishing of the open part is the mathematical statement of the linked-cluster theorem [54,57,58,61–64]:

$$(H\Omega_\Phi)_{\mathrm{op,cn}} = 0. \tag{28}$$

C. Rayleigh-Schrödinger perturbation theory and the Bloch equation

For a perturbative treatment, we partition the Hamiltonian into a zeroth-order Hamiltonian H_0 and a perturbation V:

$$H = H_0 + V. \tag{29}$$

Substituting this expression into the operator form of the Bloch equation [65],

$$H\Omega_\Phi P_\Phi = \Omega_\Phi P_\Phi H \Omega_\Phi P_\Phi, \tag{30}$$

gives [62,66,67]

$$(E_0 - H_0)\Omega_\Phi P_\Phi = Q_\Phi (V\Omega_\Phi - \Omega_\Phi P_\Phi V \Omega_\Phi) P_\Phi, \tag{31}$$

where intermediate normalization, given by Eq. (8), is required.

In order to solve the above equation, the wave operator Ω_Φ is partitioned into an order-by-order expansion:

$$\Omega_\Phi = \Omega_\Phi^{(0)} + \Omega_\Phi^{(1)} + \Omega_\Phi^{(2)} + \cdots. \tag{32}$$

Substituting this expression into Eq. (31) and equating the individual orders gives [54,66]

$$(E_0 - H_0)\Omega_\Phi^{(n)} P_\Phi = Q_\Phi \left[V\Omega_\Phi^{(n-1)} - \sum_{m=1}^{n-1} \Omega_\Phi^{(n-m)} P_\Phi V \Omega_\Phi^{(m-1)} \right] P_\Phi, \tag{33}$$

where the second term on the right side does not appear for $(n=1)$.

Now let the zeroth-order Hamiltonian be a one-body operator:

$$H_0 = \sum_{ij} \epsilon_{ij} a_i^\dagger a_j, \tag{34}$$

and this operator is defined by its matrix elements; we choose them by requiring the following relation to be satisfied:

$$\epsilon_{ij} = \epsilon_{ji} = \epsilon_{ij}^\Phi, \tag{35a}$$

where

$$\epsilon_{wr}^\Phi = 0, \tag{35b}$$

$$\epsilon_{wx}^\Phi = \langle \psi_w | \hat{f}_o^\Phi | \psi_x \rangle, \tag{35c}$$

$$\epsilon_{rs}^\Phi = \langle \psi_r | \hat{f}_u^\Phi | \psi_s \rangle, \tag{35d}$$

and the one-body operators, $\hat{f}_o^\Phi$ and $\hat{f}_u^\Phi$, are determined by the reference state $|\Phi\rangle$, but the dependence of $\hat{f}_o^\Phi$ and $\hat{f}_u^\Phi$ upon $|\Phi\rangle$ is at our disposal. The orbital subspaces are, again, defined by Eqs. (6).

Using the above choice, our zeroth-order Hamiltonian becomes

$$H_0^\Phi = \sum_{w,x \in \{\psi_o \rightarrow \Phi\}} \epsilon_{wx}^\Phi a_w^\dagger a_x + \sum_{r,s \in \{\psi_u \rightarrow \Phi\}} \epsilon_{rs}^\Phi a_r^\dagger a_s, \tag{36}$$

where the appended Φ superscript indicates that H_0^Φ now depends on the reference state $|\Phi\rangle$, and this state is at our disposal.

A diagonal form for our one-body operator H_0^Φ is obtained by requiring its orbital sets—$\{\psi_o \rightarrow \Phi\}$ and $\{\psi_u \rightarrow \Phi\}$—to satisfy the following conditions:

$$\langle \psi_w | \hat{f}_o^\Phi | \psi_x \rangle = \delta_{wx} \epsilon_w^\Phi, \tag{37a}$$

$$\langle \psi_r | \hat{f}_u^\Phi | \psi_s \rangle = \delta_{rs} \epsilon_r^\Phi, \tag{37b}$$

where, henceforth, we denote these particular sets of orbitals by $\{\psi_o \leftarrow \Phi, \hat{f}_o^\Phi\}$ and $\{\psi_u \leftarrow \Phi, \hat{f}_u^\Phi\}$, indicating that they are uniquely determined by $|\Phi\rangle$ and their one-particle operators $\hat{f}_o^\Phi$ and $\hat{f}_u^\Phi$.

Using these orbitals, H_0^Φ can be written as

$$H_0^\Phi = \sum_{w \in \{\psi_o \leftarrow \Phi, \hat{f}_o^\Phi\}} \epsilon_w^\Phi a_w^\dagger a_w + \sum_{r \in \{\psi_u \leftarrow \Phi, \hat{f}_u^\Phi\}} \epsilon_r^\Phi a_r^\dagger a_r, \tag{38}$$

and our partitioning is

$$H = H_0^\Phi + V_\Phi. \tag{39}$$

When the zeroth-order Hamiltonian is in the diagonal, one-body form, as in Eq. (38), it can be shown that the wave operator Ω_Φ satisfies a *linked diagram theorem* [54,62]:

$$(E_0 - H_0^\Phi)\Omega_\Phi P_\Phi = Q_\Phi (V_\Phi \Omega_\Phi)_{\mathrm{l}} P_\Phi, \tag{40}$$

where the individual orders, defined by Eq. (32), satisfy

$$(E_0 - H_0^\Phi)\Omega_\Phi^{(n)} P_\Phi = Q_\Phi (V_\Phi \Omega_\Phi^{(n-1)})_{\mathrm{l}} P_\Phi, \tag{41}$$

and the additional l subscripts indicate that only the linked portions contribute—all disconnected terms are open.

In order to solve Eq. (40), the wave operator Ω_Φ is written as a sum of one-, two-, and higher-body excitations,

$$\Omega_\Phi = 1 + \Omega_1^\Phi + \Omega_2^\Phi + \Omega_3^\Phi + \cdots, \tag{42}$$

where the individual amplitudes are given by expressions that are similar to Eqs. (25), for example,

$$\Omega_1^\Phi = \sum_{rw} x_{rw}^\Phi a_r^\dagger a_w. \tag{43}$$

As in the cluster operator S_Φ, the wave operator Ω_Φ and its amplitudes Ω_n^Φ are invariant to a unitary transformation of its occupied, $\{\psi_o \rightarrow \Phi\}$, or its virtual orbitals, $\{\psi_u \rightarrow \Phi\}$.

III. BRILLOUIN-BRUECKNER CONDITION

Consider the Slater determinantal state, say $|\Theta\rangle$, that satisfies the Brillouin-Brueckner condition [26,24,38,68,69]:

$$\langle \Theta_w^r | H | \Psi \rangle = 0, \tag{44}$$

for any single excitation from $|\Theta\rangle$:

$$|\Theta_w^r\rangle = a_r^\dagger a_w|\Theta\rangle, \tag{45}$$

where both the occupied and virtual orbitals determine the Brueckner determinantal-state $|\Theta\rangle$:

$$\psi_w \in \{\psi_o \to \Theta\}, \tag{46a}$$

$$\psi_r \in \{\psi_u \to \Theta\}. \tag{46b}$$

Using Eqs. (1) and (44), it is easily demonstrated that the wave function $|\Psi\rangle$ contains no single excitations from $|\Theta\rangle$:

$$\frac{1}{\mathcal{E}}\langle\Theta_w^r|H|\Psi\rangle = \langle\Theta_w^r|\Psi\rangle = 0. \tag{47}$$

Furthermore, since the single excited states $|\Theta_w^r\rangle$ are linearly independent, the wave function satisfies the following condition:

$$P_{11}^{\Theta}|\Psi\rangle = 0, \tag{48}$$

where the projector for the singly excited states is

$$P_{11}^{\Theta} = \sum_{w\in\{\psi_o\to\Theta\}}\ \sum_{r\in\{\psi_u\to\Theta\}} |\Theta_w^r\rangle\langle\Theta_w^r|, \tag{49}$$

and this subspace is completely determined by $|\Theta\rangle$; P_{11}^{Θ} is also invariant to a unitary transformation of occupied, or virtual, orbitals [30].

Using Eqs. (48) and (49), Eq. (44) can be generalized:

$$P_{11}^{\Theta}H(1-P_{11}^{\Theta})|\Psi\rangle = 0. \tag{50}$$

The occupied set of orbitals $\{\psi_o \to \Theta\}$ that satisfy Eq. (50) are called Brueckner orbitals. However, since these orbitals are invariant to a unitary transformation, Eq. (50) actually defines the Brueckner-determinantal state $|\Theta\rangle$, where $|\Theta\rangle$ determines P_{11}^{Θ}.

A coupled cluster variant of equation (50) is obtained by first noting the following identities:

$$\Omega_1^{\Theta} = 0, \tag{51a}$$

$$S_1^{\Theta} = 0, \tag{51b}$$

where the first identity is obtained by substituting Eq. (5) into Eq. (48) and using Eqs. (42) and (43) for $(\Phi=\Theta)$; the second identity uses Eqs. (24a), (24b), and (25). Therefore, from Eq. (51b), we have

$$\Omega_{\Theta} = e^{-S_1^{\Theta}}\Omega_{\Theta}. \tag{52}$$

Multiplying this equation from the right by $|\Theta\rangle$ and using Eq. (5) gives

$$|\Psi\rangle = e^{-S_1^{\Theta}}|\Psi\rangle. \tag{53}$$

Substituting this equation into Eq. (44), and using Eq. (49), we get

$$P_{11}^{\Theta}He^{-S_1^{\Theta}}|\Psi\rangle = 0. \tag{54}$$

This equation is the Brillouin-Brueckner condition for coupled cluster theory [30]. As in Eq. (50), the Brueckner orbitals that satisfy Eq. (54) are invariant to a unitary transformation, so Eq. (54) defines the determinantal state $|\Theta\rangle$, where $|\Theta\rangle$ determines P_{11}^{Θ} and S_1^{Θ}.

IV. TRIAL WAVE FUNCTIONS AND ENERGY FUNCTIONALS

A. General requirements

Consider four trial wave functions, denoted by $|\Psi_\Phi^{(\eta)}\rangle$, where $\eta=\mathrm{I}$, II, III, and IV. Each of these four states depends on the reference state $|\Phi\rangle$, satisfies intermediate normalization,

$$\langle\Phi|\Psi_\Phi^{(\eta)}\rangle = 1, \tag{55}$$

has no components within the singly excited subspace,

$$|\Psi_\Phi^{(\eta)}\rangle = (1-P_{11}^{\Phi})|\Psi_\Phi^{(\eta)}\rangle, \tag{56}$$

and yields the exact state of interest when $|\Phi\rangle$ is the Brueckner determinantal state:

$$|\Psi_\Theta^{(\eta)}\rangle = |\Psi\rangle. \tag{57}$$

Substituting Eq. (57) into Eq. (50), and using Eq. (56) for $(|\Phi\rangle=|\Theta\rangle)$, gives the Brillouin-Brueckner condition for the trial wave functions:

$$P_{11}^{\Theta}H|\Psi_\Theta^{(\eta)}\rangle = 0. \tag{58}$$

From the trial wave functions $|\Psi_\Phi^{(\eta)}\rangle$, we can construct nonvariational energy functionals

$$E_\eta[\Phi] = \langle\Phi|H|\Psi_\Phi^{(\eta)}\rangle = E_1[\Phi] + E_{\mathrm{co}}^{(\eta)}[\Phi], \tag{59}$$

where the correlation (co) energy functionals are given by

$$E_{\mathrm{co}}^{(\eta)}[\Phi] = \langle\Phi|H|\Psi_{Q_\Phi}^{(\eta)}\rangle; \tag{60}$$

the trial correlation functions are given by

$$|\Psi_{Q_\Phi}^{(\eta)}\rangle = Q_\Phi|\Psi_\Phi^{(\eta)}\rangle, \tag{61}$$

and $E_1[\Phi]$ is given by Eq. (10). Operating on Eq. (57) by Q_Θ and using Eqs. (14) and (61), we have

$$|\Psi_{Q_\Theta}^{(\eta)}\rangle = |\Psi_{Q_\Theta}\rangle. \tag{62}$$

Let us also define XC energy functionals

$$E_{\mathrm{xc}}^{(\eta)}[\Phi] = E_{\mathrm{co}}^{(\eta)}[\Phi] - E_{\mathrm{x}}[\Phi], \tag{63}$$

where the exchange energy $E_x[\Phi]$ is given by Eq. (23).

Equations (9), (57), and (59), indicate that the energy functionals $E_\eta[\Phi]$ yield the exact energy $\mathcal{E}$ when the reference state $|\Phi\rangle$ is the Brueckner determinantal state $|\Theta\rangle$

$$\mathcal{E} = E_\eta[\Theta], \tag{64}$$

and from Eqs. (13), (22), (60), (61), and (63), the following identities are obtained for the correlation and exchange-correlation energies, $\mathcal{E}_{co}[\Theta]$ and $E_{xc}[\Theta]$:

$$\mathcal{E}_{\mathrm{co}}[\Theta] = E_{\mathrm{co}}^{(\eta)}[\Theta], \tag{65}$$

$$\mathcal{E}_{\mathrm{xc}}[\Theta] = E_{\mathrm{xc}}^{(\eta)}[\Theta]. \tag{66}$$

As in the correlation energy, given by Eq. (18), the correlation-energy functionals, given by Eq. (60), can be written as

$$E_{\rm co}^{(\eta)}[\Phi] = (H\chi_\Phi^\eta)_{\rm cl}, \tag{67}$$

where the trial correlation operators χ_Φ^η generate the trial correlation functions:

$$\chi_\Phi^\eta|\Phi\rangle = |\Psi_{Q_\Phi}^{(\eta)}\rangle. \tag{68}$$

Substituting Eqs. (18) and (67) into Eq. (65) for ($|\Phi\rangle = |\Theta\rangle$), we get

$$\chi_\Theta^\eta = \chi_\Theta, \tag{69}$$

and this expression indicates that we can use any of the trial correlation operators—$\chi_\Theta^{\rm I}$, $\chi_\Theta^{\rm I}$, $\chi_\Theta^{\rm III}$, and $\chi_\Theta^{\rm IV}$—to obtain the Brueckner one, χ_Θ.

We now define the explicit forms of these trial wave functions and give expressions for their correlation-energy functionals.

B. The first trial wave function

The first trial wave function is given by

$$|\Psi_\Phi^{(\rm I)}\rangle = (1 - P_{11}^\Phi)|\Psi\rangle. \tag{70}$$

It follows from Eqs. (42) and (43) that Ω_1^Φ exclusively generates the singly excited portion of the orthogonal space:

$$P_{11}^\Phi\Omega_1^\Phi|\Phi\rangle = \Omega_1^\Phi|\Phi\rangle, \tag{71a}$$

$$P_{11}^\Phi\Omega_n^\Phi|\Phi\rangle = 0, \quad n \neq 1; \tag{71b}$$

therefore, this trial wave function can be written as

$$|\Psi_\Phi^{(\rm I)}\rangle = (\Omega_\Phi - \Omega_1^\Phi)|\Phi\rangle. \tag{72}$$

Using this expression and Eq. (19), after substituting Eq. (61) into Eq. (60), yields the first correlation-energy functional

$$E_{\rm co}^{(\rm I)}[\Phi] = [H(\chi_\Phi - \Omega_1^\Phi)]_{\rm cl}, \tag{73}$$

where we have used the following identity:

$$P_\Phi(\chi_\Phi - \Omega_1^\Phi)|\Phi\rangle = 0. \tag{74}$$

C. The second trial wave function

The second trial wave function is given by

$$|\Psi_\Phi^{(\rm II)}\rangle = e^{-S_1^\Phi}|\Psi\rangle. \tag{75}$$

Using Eqs. (5) and (24a), this equation becomes

$$|\Psi_\Phi^{(\rm II)}\rangle = e^{(S_\Phi - S_1^\Phi)}|\Phi\rangle, \tag{76}$$

where we have used the identity, given by

$$e^{-S_1^\Phi}\Omega_\Phi = e^{(S_\Phi - S_1^\Phi)}, \tag{77}$$

and this relation follows from Eqs. (24a) and (24b), since S_Φ and S_1^Φ commute.

Using Eq. (76) after substituting Eq. (61) into Eq. (60) gives the second correlation-energy functional

$$E_{\rm co}^{(\rm II)}[\Phi] = \Big[H\Big(e^{(S_\Phi - S_1^\Phi)} - 1\Big)\Big]_{\rm cl}, \tag{78}$$

where we have used the following identity:

$$\langle\Phi|HP_\Phi e^{(S_\Phi - S_1^\Phi)}|\Phi\rangle - \langle\Phi|H|\Phi\rangle = 0. \tag{79}$$

D. The third trial wave function

The third trial wave function $|\Psi_\Phi^{(\rm III)}\rangle$ can be generated by its wave operator:

$$\hat\Omega_\Phi|\Phi\rangle = |\Psi_\Phi^{(\rm III)}\rangle, \tag{80}$$

which can be expressed in an exponential form,

$$\hat\Omega_\Phi = e^{\hat S_\Phi} = 1 + \hat S_\Phi + \frac{1}{2!}\hat S_\Phi^2 + \frac{1}{3!}\hat S_\Phi^3 + \cdots, \tag{81a}$$

where $\hat S_\Phi$ can be written as a sum of n-body excitations, with the exclusion of a one-body operator:

$$\hat S_\Phi = \hat S_2^\Phi + \hat S_3^\Phi + \cdots. \tag{81b}$$

The individual amplitudes are defined by the following equations:

$$\hat S_2^\Phi = \frac{1}{2!}\sum_{rwsx}\hat s_{rwsx}^\Phi a_r^\dagger a_s^\dagger a_x a_w, \tag{82a}$$

$$\hat S_3^\Phi = \frac{1}{3!}\sum_{rwsxty}\hat s_{rwsxty}^\Phi a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w, \tag{82b}$$

where the orbital convention, Eqs. (6), remains valid.

Using Eqs. (80) and (81a), after substituting Eq. (61) into Eq. (60), gives the third correlation-energy functional

$$E_{\rm co}^{(\rm III)}[\Phi] = [H(e^{\hat S_\Phi} - 1)]_{\rm cl}, \tag{83}$$

where we have used the following:

$$\langle\Phi|HP_\Phi e^{\hat S_\Phi}|\Phi\rangle - \langle\Phi|H|\Phi\rangle = 0. \tag{84}$$

We define $\hat\Omega_\Phi$ as a solution to the following variant of Eq. (28):

$$(1 - P_{11}^\Phi)(H\hat\Omega_\Phi)_{\rm op,cn} = 0, \tag{85}$$

which defines the trial functional $|\Psi_\Phi^{(\rm III)}\rangle$ using Eq. (80).

Additional relations for the third trial wave function are presented in Appendix B, including demonstrating that $|\Psi_\Phi^{(\rm III)}\rangle$ is a valid trial wave function: Eq. (57) and the other relations from Sec. IV A are satisfied.

E. The fourth trial wave function

The fourth trial wave function is a solution of the Schödinger equation within the subspace that neglects the singly excited states:

$$(1 - P_{11}^{\Phi})H|\Psi_{\Phi}^{(\mathrm{IV})}\rangle = E_{\mathrm{IV}}[\Phi]|\Psi_{\Phi}^{(\mathrm{IV})}\rangle. \tag{86}$$

From the variational theorem, it follows that the above energy functional provides an upper bound to the exact energy:

$$E_{\mathrm{IV}}[\Phi] \geqslant \mathcal{E}. \tag{87}$$

Appendix C gives some additional relations and proves that the trial wave function and energy satisfy Eqs. (57) and (64), for $\eta = \mathrm{IV}$.

V. EXACT FOCK OPERATORS

Consider generalized, or exact, Fock operators $\hat{\mathcal{F}}_{\Phi}^{(\eta)}$ that are defined, in part, by the following matrix elements:

$$\langle\psi_r|\hat{\mathcal{F}}_{\Phi}^{(\eta)}|\psi_w\rangle = \langle\Phi_w^r|H|\Psi_{\Phi}^{(\eta)}\rangle, \quad \eta = \mathrm{I,II,III,IV}, \tag{88}$$

where the w and r orbitals are occupied and unoccupied within $|\Phi\rangle$, respectively, as noted by Eqs. (6). By multiplying Eq. (58) from the left by $\langle\Theta_w^r|$, using Eq. (49), and comparing the resulting relation to the above equation, we have

$$\langle\psi_r|\hat{\mathcal{F}}_{\Theta}^{(\eta)}|\psi_w\rangle = 0, \tag{89}$$

where the orbitals are defined by Eq. (46). When satisfied by all orbitals, this expression is equivalent to the Brillouin-Brueckner condition, given by Eq. (58).

Inserting the identity operator—defined by Eq. (15)—into Eq. (88), and using Eq. (55), we have

$$\langle\psi_r|\hat{\mathcal{F}}_{\Phi}^{(\eta)}|\psi_w\rangle = \langle\Phi_w^r|H|\Phi\rangle + \langle\Phi_w^r|H|\Psi_{Q_\Phi}^{(\eta)}\rangle, \tag{90}$$

where the trial-correlation functions $|\Psi_{Q_\Phi}^{(\eta)}\rangle$ are given by Eq. (61); the first term on the right side of Eq. (90) is the off-diagonal block of the Fock operator $\hat{F}_\Phi$:

$$\langle\psi_r|\hat{F}_{\Phi}|\psi_w\rangle = \langle\Phi_w^r|H|\Phi\rangle, \tag{91}$$

and this operator is given by

$$\hat{F}_\Phi = -\frac{1}{2}\nabla^2 + v + J_\Phi - K_\Phi, \tag{92}$$

where the Coulomb and exchange operators are given by Eqs. (11) and (12).

Let the second term on the right side of Eq. (90) define the off-diagonal block of correlation potentials $v_{\mathrm{co}}^{\Phi\eta}(\mathbf{x})$:

$$\langle\psi_r|v_{\mathrm{co}}^{\Phi\eta}|\psi_w\rangle = \langle\Phi_w^r|H|\Psi_{Q_\Phi}^{(\eta)}\rangle. \tag{93}$$

Similarly, exchange-correlation potentials $v_{\mathrm{xc}}^{\Phi\eta}(\mathbf{x})$ are defined, in part, by

$$\langle\psi_r|v_{\mathrm{xc}}^{\Phi\eta}|\psi_w\rangle = \langle\psi_r|v_{\mathrm{co}}^{\Phi\eta}|\psi_w\rangle - \langle\psi_r|K_\Phi|\psi_w\rangle. \tag{94}$$

Using Eqs. (90), (91), and (93), and with no loss of generality, our exact Fock operators $\hat{\mathcal{F}}_{\Phi}^{(\eta)}$ can be written as

$$\hat{\mathcal{F}}_{\Phi}^{(\eta)} = \hat{F}_\Phi + v_{\mathrm{co}}^{\Phi\eta}. \tag{95}$$

Multiplying Eq. (95) from the left and right by $\langle\psi_r|$ and $|\psi_w\rangle$, and using the one-body partitioning method of Eqs. (A2), gives

$$\langle\psi_r|\hat{\mathcal{F}}_{\Phi}^{(\eta)}|\psi_w\rangle = \langle\psi_r|(\hat{F}_\Phi)_{\mathrm{ex}}|\psi_w\rangle + \langle\psi_r|(v_{\mathrm{co}}^{\Phi\eta})_{\mathrm{ex}}|\psi_w\rangle; \tag{96}$$

the Brillouin-Brueckner condition (89) becomes

$$(\hat{\mathcal{F}}_\Theta)_{\mathrm{ex}} = 0, \tag{97}$$

where

$$\hat{\mathcal{F}}_\Theta = \hat{F}_\Theta + v_{\mathrm{co}}^{\Theta}, \tag{98}$$

and the η superscript is suppressed, since from Eqs. (93), (68), and (69), we have

$$(v_{\mathrm{co}}^{\Theta\eta})_{\mathrm{ex}} = (v_{\mathrm{co}}^{\Theta\eta'})_{\mathrm{ex}} = (v_{\mathrm{co}}^{\Theta})_{\mathrm{ex}}. \tag{99}$$

The remaining matrix elements of $v_{\mathrm{co}}^{\Phi\eta}$—$[\psi_w|v_{\mathrm{co}}^{\Phi\eta}|\psi_x]$ and $\langle\psi_r|v_{\mathrm{co}}^{\Phi\eta}|\psi_s]$ are at our disposal. By defining these matrix elements in a manner that is independent of η, but dependent on $|\Phi\rangle$, $v_{\mathrm{co}}^{\Theta}(\mathbf{x})$ and $\hat{\mathcal{F}}_\Theta$ are completely and unambiguously determined; our exact Fock operator can be diagonalized:

$$\hat{\mathcal{F}}_\Theta \psi_i^\Theta(\mathbf{x}) = \varepsilon_i^\Theta \psi_i^\Theta(\mathbf{x}), \tag{100}$$

where orbital energies ε_i^Θ can be defined to give exact ionization potentials and electron affinities—exact Koopman's theorems [21,70].

Since the operators presented in Eqs. (35a), $\hat{f}_o^\Phi$ and $\hat{f}_u^\Phi$ (that define H_0^Φ), and the exact Fock operators $\hat{\mathcal{F}}_{\Phi}^{(\eta)}$ are not mutually exclusive, one tempting choice is

$$\hat{\mathcal{F}}_{\Phi}^{(\eta)} = \hat{f}_o^\Phi = \hat{f}_u^\Phi. \tag{101}$$

For the remainder of this section, we obtain some additional relations involving the exact Fock operators $\hat{\mathcal{F}}_{\Phi}^{(\eta)}$ and relate the correlation potentials $v_{\mathrm{co}}^{\Phi\eta}(\mathbf{x})$ to the trial correlation-operators χ_Φ^η.

Returning to Eq. (89), we have

$$\hat{\kappa}_\Theta \hat{\mathcal{F}}_{\Theta}^{(\eta)} \hat{\gamma}_\Theta = 0, \tag{102}$$

where $\hat{\gamma}_\Phi$ is the one-particle, density-matrix operator for the determinantal state $|\Phi\rangle$ [71–74],

$$\hat{\gamma}_\Phi = \sum_{x \in \{\psi_o \to \Phi\}} |\psi_x\rangle\langle\psi_x|; \tag{103}$$

$\hat{\kappa}_\Phi$ is the projector into the virtual-orbital subspace:

$$\hat{\kappa}_\Phi = \sum_{r \in \{\psi_u \to \Phi\}} |\psi_r\rangle\langle\psi_r|, \tag{104}$$

and the identity operator $\hat{I}$ can be expressed as

$$\hat{I} = \hat{\gamma}_\Phi + \hat{\kappa}_\Phi. \tag{105}$$

Multiplying Eq. (102) from the left and right by $\langle\psi_r|$ and $|\psi_w\rangle$ gives Eq. (89).

Since all of our generalized Fock operators—$\hat{\mathcal{F}}_{\Theta}^{(\mathrm{I})}$, $\hat{\mathcal{F}}_{\Theta}^{(\mathrm{II})}$, $\hat{\mathcal{F}}_{\Theta}^{(\mathrm{III})}$, and $\hat{\mathcal{F}}_{\Theta}^{(\mathrm{IV})}$—satisfy Eq. (102), any one can be used to define an exact Fock operator $\hat{\mathcal{F}}_{\Theta}$:

$$\hat{\kappa}_{\Theta}\hat{\mathcal{F}}_{\Theta}\hat{\gamma}_{\Theta} = \hat{\kappa}_{\Theta}\hat{\mathcal{F}}_{\Theta}^{(\eta)}\hat{\gamma}_{\Theta} = \hat{\kappa}_{\Theta}\hat{\mathcal{F}}_{\Theta}^{(\eta')}\hat{\gamma}_{\Theta}, \tag{106}$$

and the Brillouin-Brueckner condition, Eq. (102), becomes

$$\hat{\kappa}_{\Theta}\hat{\mathcal{F}}_{\Theta}\hat{\gamma}_{\Theta} = 0. \tag{107}$$

Using Eq. (105), this equation can be written as

$$(\hat{I} - \hat{\gamma}_{\Theta})\hat{\mathcal{F}}_{\Theta}\hat{\gamma}_{\Theta} = 0. \tag{108}$$

Since $\hat{\gamma}_{\Theta}$ is idempotent,

$$\hat{\gamma}_{\Theta}\hat{\gamma}_{\Theta} = \hat{\gamma}_{\Theta}, \tag{109}$$

Eq. (108) can be expressed as

$$(\hat{\mathcal{F}}_{\Theta}\hat{\gamma}_{\Theta} - \hat{\gamma}_{\Theta}\hat{\mathcal{F}}_{\Theta})\hat{\gamma}_{\Theta} = 0. \tag{110}$$

By requiring $\hat{\mathcal{F}}_{\Theta}$ to be, at least in part, Hermitian,

$$\hat{\gamma}_{\Theta}\hat{\mathcal{F}}_{\Theta}\hat{\kappa}_{\Theta} = 0 \tag{111}$$

yields the following identity:

$$(\hat{\mathcal{F}}_{\Theta}\hat{\gamma}_{\Theta} - \hat{\gamma}_{\Theta}\hat{\mathcal{F}}_{\Theta})\hat{\kappa}_{\Theta} = 0. \tag{112}$$

Using Eq. (105) and adding together Eqs. (110) and (112) indicates that $\hat{\gamma}_{\Theta}$ and $\hat{\mathcal{F}}_{\Theta}$ commute:

$$[\hat{\mathcal{F}}_{\Theta}, \hat{\gamma}_{\Theta}] = 0. \tag{113}$$

Equation (113) is a generalization of the one obtained for Hartree-Fock theory [2,49,50].

Note that for any reference state, say $|\Phi'\rangle$, we can find a corresponding state, $|\Phi\rangle$, in which the following relation is satisfied:

$$\hat{\kappa}_{\Phi}\hat{\mathcal{F}}_{\Phi'}^{(\eta)}\hat{\gamma}_{\Phi} = 0. \tag{114}$$

Solving this expression in an iterative and self-consistent-field manner leads to the Brillouin-Brueckner condition, Eq. (107), being satisfied, since when $|\Phi\rangle = |\Phi'\rangle$, we have $|\Phi\rangle = |\Theta\rangle$.

Consider now the following application of the identity operator:

$$\hat{\mathcal{F}}_{\Phi}|\psi_w\rangle = \hat{I}\hat{\mathcal{F}}_{\Phi}|\psi_w\rangle = \sum_{x \in \{\psi_o \rightarrow \Phi\}} \varepsilon_{xw}^{\Phi}|\psi_x\rangle + \sum_{r \in \{\psi_u \rightarrow \Phi\}} \varepsilon_{rw}^{\Phi}|\psi_r\rangle, \tag{115}$$

where

$$\varepsilon_{ij}^{\Phi} = \langle\psi_i|\hat{\mathcal{F}}_{\Phi}|\psi_j\rangle. \tag{116}$$

Setting $\Phi = \Theta$, and using Eq. (89), gives exact Hartree-Fock equations

$$\hat{\mathcal{F}}_{\Theta}|\psi_w\rangle = \sum_{x \in \{\psi_o \rightarrow \Theta\}} \varepsilon_{xw}^{\Theta}|\psi_x\rangle, \tag{117}$$

where the orbital $|\psi_w\rangle$ is also from the set $\{\psi_o \rightarrow \Theta\}$.

Returning to Eq. (90), and using Eqs. (91) and (68), we have

$$\begin{aligned}\langle\psi_r|\hat{\mathcal{F}}_{\Phi}^{(\eta)}|\psi_w\rangle &= \langle\psi_r|\hat{F}_{\Phi}|\psi_w\rangle + \langle\Phi_w^r|H\chi_{\Phi}^{\eta}|\Phi\rangle \\ &= \langle\psi_r|(\hat{F}_{\Phi})_{\mathrm{op}}|\psi_w\rangle + \langle\psi_r|[(H\chi_{\Phi}^{\eta})_1]_{\mathrm{op}}|\psi_w\rangle,\end{aligned} \tag{118}$$

where we use the more restrictive definition of an open (op) operator, presented in Appendix A.

Setting $(\Phi = \Theta)$, and using Eqs. (69) and (89), gives another variant of the Brillouin-Brueckner condition

$$[\hat{F}_{\Theta} + (H\chi_{\Theta})_1]_{\mathrm{op}} = 0, \tag{119}$$

where this expression acts within the one-body sector of the Hilbert space, even though the subscript, op, indicates the open portion, defined by the N-body sector.

Comparing Eq. (118) with Eq. (96), and using Eq. (A8), we have

$$(v_{\mathrm{co}}^{\Phi\eta})_{\mathrm{ex}} = [(H\chi_{\Phi}^{\eta})_1]_{\mathrm{op}}. \tag{120}$$

By using this relation, diagrammatic expansions for $(v_{\mathrm{co}}^{\Phi\eta})_{\mathrm{ex}}$ can be obtained that are a subset of the open, one-body diagrams of $H\chi_{\Phi}$ [55].

VI. FUNCTIONALS OF THE ONE-PARTICLE DENSITY MATRIX γ

It is well known that there is a one-to-one correspondence between the set of determinant states $\{|\Phi\rangle\}$ and their one-particle density matrices [2,50] $\{\gamma\}$, where these density-matrices are given by [49,71–74]

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_{w \in \{\psi_o \rightarrow \Phi\}} \psi_w(\mathbf{x})\psi_w^*(\mathbf{x}'). \tag{121}$$

Because of this correspondence, determinantal states are uniquely determined by their one-particle density matrix: $|\Phi(\gamma)\rangle$; functionals, or functions, that depend on $|\Phi\rangle$ can be written as ones depending on γ. For example, the total energy $\mathcal{E}$, Eq. (9), and our energy functionals $E_{\eta}[\Phi]$, Eq. (59), can be written in the following manner:

$$\mathcal{E} = E_1[\gamma] + \mathcal{E}_{\mathrm{co}}[\gamma], \tag{122}$$

$$E_{\eta}[\gamma] = E_1[\gamma] + E_{\mathrm{co}}^{(\eta)}[\gamma], \tag{123}$$

and, in addition, our trial wave functions $|\Psi_{\Phi(\gamma)}^{(\eta)}\rangle$ can be denoted by $|\Psi_{\gamma}^{(\eta)}\rangle$.

For simplicity, we require the external potential $v(\mathbf{r})$ to be a spin-free operator, so the first-order energy—Eqs. (10)–(12)—can be written as

$$E_1[\gamma] = \int \left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 \gamma(\mathbf{x},\mathbf{x}') \right]_{\mathbf{x}'=\mathbf{x}} d\mathbf{x} + \int v(\mathbf{r})\gamma(\mathbf{x},\mathbf{x})d\mathbf{x} + E_{\mathrm{J}}[\gamma] - E_{\mathrm{x}}[\gamma], \tag{124}$$

where the Coulomb and exchange energies are

$$E_{\mathrm{J}}[\gamma] = \frac{1}{2}\int\int r_{12}^{-1}\gamma(\mathbf{x}_1,\mathbf{x}_1)\gamma(\mathbf{x}_2,\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2, \tag{125}$$

$$E_x[\gamma] = \frac{1}{2}\int\int r_{12}^{-1}\gamma(\mathbf{x}_1,\mathbf{x}_2)\gamma(\mathbf{x}_2,\mathbf{x}_1)d\mathbf{x}_1 d\mathbf{x}_2, \tag{126}$$

and an integration over $\mathbf{x}_i$ implies a summation over the spin variable ω_i and an integration over the spatial portion $\mathbf{r}_i$.

Similarly, the one-body operators $\hat{\mathcal{F}}_{\Phi}^{(\eta)}$, Eq. (95), can be written as

$$\hat{\mathcal{F}}_{\gamma}^{(\eta)} = \hat{F}_{\gamma} + v_{\mathrm{co}}^{\gamma\eta}, \tag{127}$$

where, instead of Eq. (92), the Fock operator is given by

$$\hat{F}_{\gamma} = -\frac{1}{2}\nabla^2 + v + J_{\gamma} - K_{\gamma}, \tag{128}$$

and the Coulomb J_γ and exchange K_γ operators satisfy

$$J_{\gamma}\phi(\mathbf{x}_1) = \int r_{12}^{-1}\gamma(\mathbf{x}_2,\mathbf{x}_2)\phi(\mathbf{x}_1)d\mathbf{x}_2, \tag{129}$$

$$K_{\gamma}\phi(\mathbf{x}_1) = \int r_{12}^{-1}\gamma(\mathbf{x}_1,\mathbf{x}_2)\phi(\mathbf{x}_2)d\mathbf{x}_2. \tag{130}$$

The identity operator, given by Eq. (105), can be written as

$$\hat{I} = \hat{\gamma} + \hat{\kappa}_{\gamma}, \tag{131}$$

where the density-matrix operator $\hat{\gamma}$ is defined by its kernel $\gamma(\mathbf{x},\mathbf{x}')$ [74],

$$\hat{\gamma}\phi(\mathbf{x}) = \int \gamma(\mathbf{x},\mathbf{x}')\phi(\mathbf{x}')d\mathbf{x}', \tag{132}$$

and $\kappa_\gamma(\mathbf{x},\mathbf{x}')$ is the kernel of the virtual-space projector,

$$\hat{\kappa}_{\gamma}\phi(\mathbf{x}) = \int \kappa_{\gamma}(\mathbf{x},\mathbf{x}')\phi(\mathbf{x}')d\mathbf{x}', \tag{133}$$

where

$$\kappa_{\gamma}(\mathbf{x},\mathbf{x}') = \sum_{r\in\{\psi_u\to\gamma\}} \psi_r(\mathbf{x})\psi_r^*(\mathbf{x}'), \tag{134}$$

and $\hat{\kappa}_\Phi$ is given by Eq. (104). Similarly, the one-particle density matrix for the Brueckner state, say $\tau(\mathbf{x},\mathbf{x}')$, and its density-matrix operator, say $\hat{\tau}$, are given by the following expressions:

$$\tau(\mathbf{x},\mathbf{x}') = \sum_{w\in\{\psi_o\to\Theta\}} \psi_w(\mathbf{x})\psi_w^{\dagger}(\mathbf{x}'), \tag{135}$$

$$\hat{\tau}\phi(\mathbf{x}) = \int \tau(\mathbf{x},\mathbf{x}')\phi(\mathbf{x}')d\mathbf{x}', \tag{136}$$

where we have

$$|\Theta\rangle = |\Phi(\tau)\rangle. \tag{137}$$

Since the one-particle density matrix $\hat{\tau}$ also satisfies

$$\hat{\tau} = \hat{\gamma}_{\Theta}, \tag{138}$$

where $\hat{\gamma}_\Theta$ is given by Eq. (103), the Brillouin-Brueckner condition, given by Eq. (107), and its complex conjugate, given by Eq. (111), become

$$\hat{\kappa}_{\tau}\hat{\mathcal{F}}_{\tau}\hat{\tau} = 0, \tag{139a}$$

$$\hat{\tau}\hat{\mathcal{F}}_{\tau}\hat{\kappa}_{\tau} = 0; \tag{139b}$$

furthermore, the commutation condition, Eq. (113), can be written as

$$[\hat{F}_{\tau}, \tau] = 0, \tag{140}$$

and the exact Hartree-Fock equation (117) is

$$\hat{\mathcal{F}}_{\tau}|\psi_w\rangle = \sum_{x\epsilon\{\psi_o\to\tau\}} \epsilon_{xw}^{\tau}|\psi_x\rangle, \tag{141}$$

where the occupied orbital $|\psi_w\rangle$ is also from $\{\psi_o \to \tau\}$.

In addition, the other Brillouin-Brueckner condition, Eq. (97), can be written as

$$(\hat{F}_{\tau})_{\mathrm{ex}} = 0, \tag{142}$$

where Eq. (98) becomes

$$\hat{\mathcal{F}}_{\tau} = \hat{F}_{\tau} + v_{\mathrm{co}}^{\tau}. \tag{143}$$

Elsewhere [51] we illustrate how the correlation energy and correlation-energy functionals, $\mathcal{E}_{\mathrm{co}}[\gamma]$ and $E_{\mathrm{co}}^{(\eta)}[\gamma]$, can be obtained from many-body perturbation theory, in which all terms (or diagrams) explicitly depend on γ. [An explicit expression for the first-order energy $E_1[\gamma]$ is given by Eq. (124).]

VII. APPROXIMATIONS

Density-functional theory uses a universal exchange-correlation functional, independent of the external potential, permitting approximations to be derived from model systems, where, in the vicinity of the model systems, the general form of the exchange-correlation functional is known. In contrasts, our correlation-energy functionals depend on the external potential $v(\mathbf{r})$: $E_{\mathrm{co}}^{(\eta)}[\gamma,v]$. Therefore, in this sense, these functionals are nonuniversal. Nevertheless, as demonstrated below, model systems can still be used to obtain approximations for $E_{\mathrm{co}}^{(\eta)}[\gamma,v]$.

In the approximations we consider, we often assume that the $\mathcal{E}_{\mathrm{co}}[\gamma,v]$ and $E_{\mathrm{co}}^{(\eta)}[\gamma,v]$ functionals can be expressed in a simplified form, for example, as integrals involving the coordinates of only two electrons:

$$\mathcal{E}_{\mathrm{co}}[\gamma,v]=\frac{1}{2}\int\int \mathcal{G}_{\mathrm{co}}(\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2, \tag{144a}$$

$$E_{\mathrm{co}}^{(\eta)}[\gamma,v]=\frac{1}{2}\int\int G_{\mathrm{co}}^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2, \tag{144b}$$

where the integrands, $\mathcal{G}_{\mathrm{co}}(\mathbf{x}_1,\mathbf{x}_2)$ and $G_{\mathrm{co}}^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)$, explicitly depends upon $\gamma(\mathbf{x}_1,\mathbf{x}_2)$, $\gamma(\mathbf{x}_2,\mathbf{x}_1)$, $v(\mathbf{r}_1)$, and $v(\mathbf{r}_2)$, and can include gradients or higher-order derivatives, e.g., $\nabla_1^2\gamma(\mathbf{x}_1,\mathbf{x}_2)$.

Now let $E_{\mathrm{co}}^{(\eta)}[\gamma,v]$ be known for some model system, say the helium atom, in the vicinity of some one-particle density matrix, say the Brueckner one. In that case, the following prescription yields an approximate correlation-energy functional:

$$E_{\mathrm{co}}^{(\eta)}[\gamma,v]\approx E_{\mathrm{co}}^{(\eta)}[\tau_{\mathrm{He}},v_{\mathrm{He}}]_{(\tau_{\mathrm{He}}=\gamma,v_{\mathrm{He}}=v)}, \tag{145}$$

where τ_{He} is the Brueckner, one-particle, density matrix for the helium atom and v_{He} is the external potential for this system. Using Eq. (65), we have

$$E_{\mathrm{co}}^{(\eta)}[\gamma,v]\approx \mathcal{E}_{\mathrm{co}}[\tau_{\mathrm{He}},v_{\mathrm{He}}]_{(\tau_{\mathrm{He}}=\gamma,v_{\mathrm{He}}=v)}, \tag{146}$$

or for the general case

$$E_{\mathrm{co}}^{(\eta)}[\gamma,v]\approx \mathcal{E}_{\mathrm{co}}[\tau_x,v_x]_{(\tau_x=\gamma,v_x=v)}, \tag{147}$$

where v_x is the external potential associated with a Brueckner one-particle density matrix τ_x.

In the limit of $\gamma\rightarrow\tau_x$, necessarily, many terms from $\mathcal{E}_{\mathrm{co}}[\gamma,v_x]$ must vanish [51]. Since, apparently, many, or all, of these vanishing diagrams are also excluded in the $E_{\mathrm{co}}^{(\mathrm{III})}[\gamma,v_x]$ expansion, most probably, the above approximation, Eq. (147), is most appropriate for $\eta=\mathrm{III}$:

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma,v]\approx \mathcal{E}_{\mathrm{co}}[\tau_x,v_x]_{(\tau_x=\gamma,v_x=v)}. \tag{148}$$

Furthermore, since the Brueckner density matrix for the helium atom, τ_{He}, is approximately equal to the Hartree-Fock one, say $\tilde{\tau}_{\mathrm{He}}$, for Eq. (146), we can write

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma,v]\approx \mathcal{E}_{\mathrm{co}}[\tilde{\tau}_{\mathrm{He}},v_{\mathrm{He}}]_{(\tilde{\tau}_{\mathrm{He}}=\gamma,v_{\mathrm{He}}=v)}. \tag{149}$$

Assuming that the terms arising from the helium potential v_{He} are small, neglecting to make the substitution $v_{\mathrm{He}}=v$, should yield only a small error:

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma]\approx \mathcal{E}_{\mathrm{co}}[\tilde{\tau}_{\mathrm{He}},v_{\mathrm{He}}]_{(\tilde{\tau}_{\mathrm{He}}=\gamma)}. \tag{150}$$

This assumption seems reasonable since the dominant portion of the correlation energy $\mathcal{E}_{\mathrm{co}}$ comes from electron-electron interactions and the external potential v is treated well in first order, since v is a one-body operator.

A well-known approximation for $\mathcal{E}_{\mathrm{co}}[\tilde{\tau}_{\mathrm{He}},v_{\mathrm{He}}]$ is given by the Colle and Salvetti functional [18,19], say $\mathcal{E}_{\mathrm{co}}^{\mathrm{cs}}[\tilde{\tau}_{\mathrm{He}}]$; so we have

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma]\approx \mathcal{E}_{\mathrm{co}}^{\mathrm{cs}}[\tilde{\tau}_{\mathrm{He}}]_{(\tilde{\tau}_{\mathrm{He}}=\gamma)}, \tag{151}$$

where we have suppressed any mention of v_{He}, since the Colle-Salvetti functional is universal; it has no explicit dependence on the external potential. However, this functional can still possess an implicit dependence on v_{He}, since, for example, its four empirical parameters are determined by using data from the helium atom. As an alternative to Eq. (151), an approach that fits the method more appropriately would use the approximation given by Eq. (149). Unfortunately, at this time—as far as we know—no functional exists that has an external potential dependence.

Now consider the approximation given by Eq. (148), but let the known system be an electron gas:

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma,v]\approx \mathcal{E}_{\mathrm{co}}[\tau_g,v_g]_{(\tau_g=\gamma,v_g=v)}, \quad v_g=\mathrm{const}, \tag{152}$$

where τ_g is the Brueckner, one-particle, density matrix for an electron gas and v_g is the external potential, a constant, i.e., $v_g(\mathbf{r})$ does not depend on $\mathbf{r}$. If periodic boundary conditions are used, the Brueckner orbitals—which are also Hartree-Fock orbitals—are known to be plane waves [2,52,75–77], so τ_g is known. Furthermore, it is well known that the correlation energy $\mathcal{E}_{\mathrm{co}}$ of an electron gas does not depend on its constant potential, so there is no place to make the substitution $(v_g=v)$ in the above equation. Hence, we obtain an approximation—an electron-gas approximation—that yields a universal functional

$$E_{\mathrm{co}}^{(\mathrm{III})}[\gamma]\approx \mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}[\tau_g]_{(\tau_g=\gamma)}, \tag{153}$$

where $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}$ denotes the correlation energy of an electron gas, i.e., the term on the right side of Eq. (152):

$$\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}[\gamma]=\mathcal{E}_{\mathrm{co}}[\gamma,v=\mathrm{const}], \tag{154}$$

and this definition is valid for any one-particle density matrix γ.

Equation (153) shares many similarities with the LDA of density-functional theory [2,1,7], where this approach constructs approximate energy functionals from expressions derived from a *uniform* electron gas, and this system has both an infinite volume and an infinite number of particles. In this limiting case, the density of the Brueckner reference state $|\Theta\rangle$, say ρ_{ug}, is identical to the density of the target state $|\Psi\rangle$, both being a constant; the correlation energy of a uniform electron gas, say $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}(\rho_{\mathrm{ug}})$, is a function of this density, not a functional [52,75–77]. In the LDA, a functional is constructed using the function $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}(\rho_{\mathrm{ug}})$ divided by the number of electrons—the correlation energy per particle. An analogous approach may be necessary when constructing the functional $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}[\tau_g]$, although the one-particle density matrix for an electron gas is not a constant [2,52,76]. Furthermore, when evaluating the diagrams for $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}(\rho_{\mathrm{ug}})$, as in the random-phase approximation (RPA) [52,75–77], the summations over the occupied, plane-wave states are replaced by integrals. For an exact treatment of $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}[\tau_g]$, this approach cannot be used, and, mathematically speaking, this is the difference between $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}[\tau_g]$ and $\mathcal{E}_{\mathrm{co}}^{(\mathrm{gas})}(\rho_{\mathrm{ug}})$.

We also mention that the correlation potentials v_{co}^{γ} can be treated in a similar manner as the correlation-energy functionals $E_{\mathrm{co}}^{(\eta)}[\gamma,v]$, since they also depend on the external potential $v_{\mathrm{co}}^{\gamma}[v]$. However, we now pursue a different approach, permitting correlation potentials to be obtained as functional derivatives of variation correlation-energy functionals, as in Kohn-Sham DFT.

VIII. VARIATIONAL FORMALISM

We now introduce variational energy functionals $\overline{E}_\eta[\gamma]$. By functional differentiation of these functionals with respect to the one-particle density matrix γ, generalized Fock operators are defined. These operators—denoted by $\hat{\zeta}_\tau^{(\eta)}$—satisfy the same Brillouin-Brueckner and commutation relations, Eqs. (139a) and (140), as the corresponding nonvariational ones, $\hat{\mathcal{F}}_\tau^{(\eta)}$. (A brief comparison with the *exact* self-consistent-field theory by Löwdin is presented elsewhere [51]. Lindgren and Salomonson [21] also present a variational Brueckner-orbital formalism, based on an orbital approach and many-body perturbation theory.)

Using our trial wave functions from Sec. IV, we can construct variational energy functionals

$$\overline{E}_\eta[\gamma] = \frac{\langle \Psi_\gamma^{(\eta)}|H|\Psi_\gamma^{(\eta)}\rangle}{\langle \Psi_\gamma^{(\eta)}|\Psi_\gamma^{(\eta)}\rangle} = E_1[\gamma] + \overline{E}_{\text{co}}^{(\eta)}[\gamma], \tag{155}$$

where the last relation defines the variational correlation-energy functionals $\overline{E}_{\text{co}}^{(\eta)}[\gamma]$ as $\overline{E}_\eta[\gamma] - E_1[\gamma]$, and the first-order energy $E_1[\gamma]$ is given by Eq. (124). [An alternative to Eq. (155) that exploits normal ordering is given elsewhere [51].]

Let us also define variational XC energy functionals

$$\overline{E}_{\text{xc}}^{(\eta)}[\gamma] = \overline{E}_{\text{co}}^{(\eta)}[\gamma] - E_x[\gamma], \tag{156}$$

where the exchange energy $E_x[\gamma]$ is given by Eq. (126).

The exact energy, given by Eq. (9), is also given by

$$\mathcal{E} = \frac{\langle \Psi|H|\Psi\rangle}{\langle \Psi|\Psi\rangle} = E_1[\gamma] + \mathcal{E}_{\text{co}}[\gamma], \tag{157}$$

where the last relation defines the correlation energy $\mathcal{E}_{\text{co}}[\gamma]$.

From the variational theorem, the fourth trial wave functions are equal:

$$\overline{E}_{\text{IV}}[\gamma] = E_{\text{IV}}[\gamma], \tag{158}$$

and we have

$$\overline{E}_{\text{co}}^{(\text{IV})}[\gamma] = E_{\text{co}}^{(\text{IV})}[\gamma]. \tag{159}$$

From the variational theorem, for all four cases, we also have

$$\overline{E}_\eta[\gamma] \geqslant \mathcal{E}, \tag{160}$$

where Eqs. (57), (157), (155), (156), and (22) give the following equalities that appear for the Brueckner one-particle density matrix τ:

$$\mathcal{E} = \overline{E}_\eta[\tau] = E_\eta[\tau], \tag{161}$$

$$\mathcal{E}_{\text{co}}[\tau] = \overline{E}_{\text{co}}^{(\eta)}[\tau] = E_{\text{co}}^{(\eta)}[\tau], \tag{162}$$

$$\mathcal{E}_{\text{xc}}[\tau] = \overline{E}_{\text{xc}}^{(\eta)}[\tau] = E_{\text{xc}}^{(\eta)}[\tau], \tag{163}$$

and the latter relations use Eqs. (64)–(66).

Equations (160) and (161) indicate that the minimization of $\overline{E}_\eta[\gamma]$ occurs at τ.We now pursue, in a formal way, the minimization of $\overline{E}_\eta[\gamma]$, using an approach that is similar to the procedure used by Parr and Yang [2] in their treatment of Hartree-Fock theory, where $\overline{E}_\eta[\gamma]$ is subject to the constraint that the one-particle density-matrix comes from a single-determinantal state $\gamma(|\Phi\rangle)$. This condition is imposed by requiring the one-particle density matrix γ to have a trace equal to the number of electrons N_γ, and that it is also idempotent [49,50]:

$$\int\int \gamma(\mathbf{x}_3,\mathbf{x}_4)\,\delta(\mathbf{x}_4 - \mathbf{x}_3)\,d\mathbf{x}_3 d\mathbf{x}_4 = N_\gamma, \tag{164a}$$

$$\int \gamma(\mathbf{x}_3,\mathbf{x}_5)\,\gamma(\mathbf{x}_5,\mathbf{x}_4)\,d\mathbf{x}_5 = \gamma(\mathbf{x}_3,\mathbf{x}_4). \tag{164b}$$

The normalization constraint, given by Eq. (164a), is consistent with γ being constructed from N_γ orbitals, as in Eq. (121); Eq. (164b) insures that the density-matrix operator $\hat{\gamma}$—when acting within the one-particle Hilbert space—is a projector into the occupied subspace, as indicated by Eq. (103), where γ serves as the kernel of the one-particle density-matrix operator $\hat{\gamma}$, as indicated by Eq. (132).

Using the above constraints, the variational problem is expressed as

$$\delta\mathcal{L}[\gamma]_\tau = 0, \tag{165}$$

where

$$\begin{aligned}\mathcal{L}[\gamma] = {} & \overline{E}_\eta[\gamma] - \beta\left[\int\int \gamma(\mathbf{x}_3,\mathbf{x}_4)\,\delta(\mathbf{x}_4 - \mathbf{x}_3)\,d\mathbf{x}_3 d\mathbf{x}_4 - N_\gamma\right] \\ & - \int\int d\mathbf{x}_3 d\mathbf{x}_4 \alpha(\mathbf{x}_4,\mathbf{x}_3)\left[\int \gamma(\mathbf{x}_3,\mathbf{x}_5)\,\gamma(\mathbf{x}_5,\mathbf{x}_4)\,d\mathbf{x}_5 \right. \\ & \left. - \gamma(\mathbf{x}_3,\mathbf{x}_4)\right],\end{aligned} \tag{166}$$

and where α and β are the Lagrangian multipliers. Equation (165) is satisfied when the functional derivative of $\mathcal{L}$ vanishes:

$$\left.\frac{\delta\mathcal{L}[\gamma]}{\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)}\right|_\tau = 0, \tag{167}$$

where the definition of the functional derivative is

$$\delta\mathcal{L}[\gamma] = \int\int \frac{\delta\mathcal{L}[\gamma]}{\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)}\,\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)\,d\mathbf{x}_1 d\mathbf{x}_2. \tag{168}$$

Substituting Eq. (166) into Eq. (167) yields

$$\begin{aligned}\zeta_\tau^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2) & - \int d\mathbf{x}_3[\tau(\mathbf{x}_1,\mathbf{x}_3)\alpha(\mathbf{x}_3,\mathbf{x}_2) + \alpha(\mathbf{x}_1,\mathbf{x}_3)\tau(\mathbf{x}_3,\mathbf{x}_2)] \\ & + \alpha(\mathbf{x}_1,\mathbf{x}_2) - \beta\delta(\mathbf{x}_1 - \mathbf{x}_2) = 0,\end{aligned} \tag{169}$$

where

$$\zeta_\tau^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)=\left.\frac{\delta\overline{E}_\eta[\gamma]}{\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)}\right|_\tau . \tag{170}$$

Let the two-body functions, $\alpha(\mathbf{x}_1,\mathbf{x}_2)$ and $\zeta_\tau^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)$, serve as kernels of operators, $\hat{\alpha}$ and $\hat{\zeta}_\tau^{(\eta)}$; explicitly, we have

$$\hat{\alpha}\phi(\mathbf{x}_1)=\int\alpha(\mathbf{x}_1,\mathbf{x}_2)\phi(\mathbf{x}_2)d\mathbf{x}_2, \tag{171}$$

$$\hat{\zeta}_\tau^{(\eta)}\phi(\mathbf{x}_1)=\int\zeta_\tau^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)\phi(\mathbf{x}_2)d\mathbf{x}_2. \tag{172}$$

Using this notation, the operator form of Eq. (169) is given by

$$\hat{\zeta}_\tau^{(\eta)}-\hat{\tau}\hat{\alpha}-\hat{\alpha}\hat{\tau}+\hat{\alpha}-\beta=0, \tag{173}$$

where $\hat{\tau}$ is defined by Eq. (136).

The identity operator $\hat{I}$, defined by Eq. (131), and expressed as

$$I=\hat{\tau}+\hat{\kappa}_\tau, \tag{174}$$

can be used to obtain the following relation:

$$\hat{\alpha}-\hat{\tau}\hat{\alpha}-\hat{\alpha}\hat{\tau}=I(\hat{\alpha}-\hat{\tau}\hat{\alpha}-\hat{\alpha}\hat{\tau})I=\hat{\kappa}_\tau\hat{\alpha}\hat{\kappa}_\tau-\hat{\tau}\hat{\alpha}\hat{\tau}, \tag{175}$$

which we substitute into Eq. (173); this procedure gives

$$\hat{\zeta}_\tau^{(\eta)}-\hat{\tau}\hat{\alpha}\hat{\tau}+\hat{\kappa}_\tau\hat{\alpha}\hat{\kappa}_\tau-\beta=0, \tag{176}$$

and yields the following requirements:

$$\hat{\kappa}_\tau\hat{\zeta}_\tau\hat{\tau}=0, \tag{177a}$$

$$\hat{\tau}\hat{\zeta}_\tau\hat{\kappa}_\tau=0, \tag{177b}$$

where we have dropped the η superscript since, for $(\gamma=\tau)$, all operators are equal within these blocks:

$$\hat{\kappa}_\tau\hat{\zeta}_\tau^{(\eta)}\hat{\tau}=\hat{\kappa}_\tau\hat{\zeta}_\tau^{(\eta')}\hat{\tau}=\hat{\kappa}_\tau\hat{\zeta}_\tau\hat{\tau}, \tag{178a}$$

$$\hat{\tau}\hat{\zeta}_\tau^{(\eta)}\hat{\kappa}_\tau=\hat{\tau}\hat{\zeta}_\tau^{(\eta')}\hat{\kappa}_\tau=\hat{\tau}\hat{\zeta}_\tau\hat{\kappa}_\tau. \tag{178b}$$

Equation (177a) is yet another representation of the Brillouin-Brueckner condition; comparing Eqs. (139) and (177) give

$$\hat{\kappa}_\tau\hat{\zeta}_\tau\hat{\tau}=\hat{\kappa}_\tau\hat{\mathcal{F}}_\tau\hat{\tau}, \tag{179a}$$

$$\hat{\tau}\hat{\zeta}_\tau\hat{\kappa}_\tau\cdot\ =\hat{\tau}\hat{\mathcal{F}}_\tau\hat{\kappa}_\tau, \tag{179b}$$

and it is easily verified that the commutation relation, Eq. (140), also holds for the variational one-body operators $\hat{\zeta}_\tau$:

$$[\hat{\zeta}_\tau,\hat{\tau}]=0. \tag{180}$$

An alternative to the exact Hartree-Fock equation (141) is

$$\hat{\zeta}_\tau^{(\eta)}|\psi_w\rangle=\sum_{x\in\{\psi_o\to\tau\}}\xi_{xw}^{\tau\eta}|\psi_x\rangle, \tag{181}$$

where the appended η superscripts appear since the occupied-block matrix elements $\xi_{xw}^{\tau\eta}$, perhaps, depend on η. However, we can redefine the variational operators $\hat{\zeta}_\tau^{(\eta)}$ to remove this dependence, since Eqs. (177) still holds. In any event, we assume that $\hat{\zeta}_\tau^{(\eta)}$ is independent of η and choose orbitals that diagonalize ξ_{xw}^{τ}, giving a generalized Hartree-Fock equation that is an alternative to Eq. (100):

$$\hat{\zeta}_\tau\overline{\psi}_i^\tau(\mathbf{x})=\xi_i^\tau\overline{\psi}_i^\tau(\mathbf{x}). \tag{182}$$

Substituting Eq. (155) into Eq. (170) for $\tau=\gamma$ gives

$$\zeta_\gamma^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)=F_\gamma(\mathbf{x}_1,\mathbf{x}_2)+\nu_{\text{co}}^{\gamma\eta}(\mathbf{x}_1,\mathbf{x}_2), \tag{183}$$

where

$$F_\gamma(\mathbf{x}_1,\mathbf{x}_2)=\frac{\delta E_1[\gamma]}{\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)}, \tag{184}$$

$$\nu_{\text{co}}^{\gamma\eta}(\mathbf{x}_1,\mathbf{x}_2)=\frac{\delta\overline{E}_{\text{co}}^{(\eta)}[\gamma]}{\delta\gamma(\mathbf{x}_2,\mathbf{x}_1)}, \tag{185}$$

and $F_\gamma(\mathbf{x}_1,\mathbf{x}_2)$ is the kernel of the Fock operator $\hat{F}_\gamma$:

$$F_\gamma(\mathbf{x}_1,\mathbf{x}_2)=\delta(\mathbf{x}_2-\mathbf{x}_1)\left[-\frac{1}{2}\nabla_2^2+\upsilon(\mathbf{r}_2)\right]+\delta(\mathbf{x}_2-\mathbf{x}_1)\int r_{23}^{-1}\gamma(\mathbf{x}_3,\mathbf{x}_3)d\mathbf{x}_3-r_{12}^{-1}\gamma(\mathbf{x}_1,\mathbf{x}_2); \tag{186}$$

$\nu_{\text{co}}^{\gamma\eta}(\mathbf{x}_1,\mathbf{x}_2)$ are the kernels of the variational correlation potentials $\hat{\nu}_{\text{co}}^{\gamma\eta}$.

The operator form of Eq. (183) is

$$\hat{\zeta}_\gamma^{(\eta)}=\hat{F}_\gamma+\hat{\nu}_{\text{co}}^{\gamma\eta}. \tag{187}$$

Substituting this equation into Eq. (178) indicates that we have

$$\hat{\kappa}_\tau\hat{\nu}_{\text{co}}^{\tau\eta}\hat{\tau}=\hat{\kappa}_\tau\hat{\nu}_{\text{co}}^{\tau\eta'}\hat{\tau}=\hat{\kappa}_\tau\hat{\nu}_{\text{co}}^{\tau}\hat{\tau}, \tag{188a}$$

$$\hat{\tau}\hat{\nu}_{\text{co}}^{\tau\eta}\hat{\kappa}_\tau=\hat{\tau}\hat{\nu}_{\text{co}}^{\tau\eta'}\hat{\kappa}_\tau=\hat{\tau}\hat{\nu}_{\text{co}}^{\tau}\hat{\kappa}_\tau. \tag{188b}$$

Substituting Eqs. (187) and (143) into Eq. (179) and using the two above definitions yields

$$\hat{\kappa}_\tau\hat{\nu}_{\text{co}}^{\tau}\hat{\tau}=\hat{\kappa}_\tau\upsilon_{\text{co}}^{\tau}\hat{\tau}, \tag{189a}$$

$$\hat{\tau}\hat{\nu}_{\text{co}}^{\tau}\hat{\kappa}_\tau\cdot\ =\hat{\tau}\upsilon_{\text{co}}^{\tau}\hat{\kappa}_\tau. \tag{189b}$$

In order to acquire the kernels of the generalized Fock operators $\zeta_\tau^{(\eta)}(\mathbf{x}_1,\mathbf{x}_2)$, given by Eq. (183), it is necessary to obtain the functional derivatives of $E_1[\gamma]$ and $\overline{E}_{\text{co}}^{(\eta)}[\gamma]$, as indicated by Eqs. (184) and (185). The functional derivative for $E_1[\gamma]$ can be evaluated using Eqs. (124)–(126), yielding Eq. (186). The functional derivative of the diagrammatic terms of $\overline{E}_{\text{co}}^{(\eta)}[\gamma]$ can also be obtained; the details are presented elsewhere [55]. (Here we only mention that by imposing the same occupied and virtual orbital degeneracies as in the diagrammatic expansions presented elsewhere [51], each diagram in the expansion is given by a product of one-particle density matrices, and can, therefore, be differentiated in the same manner as in the treatment of $E_1[\gamma]$. After the functional derivative is taken, the nondegeneracy of the orbitals can be restored, since the entire expansion is invariant to the choice of orbital energies, but this removes the explicit dependence on γ for each term.)

By considering Eqs. (161) and (162), it is easily determined that all approximations presented in Sec. VII are valid when $E_{\text{co}}^{(\eta)}$ is replaced by $\overline{E}_{\text{co}}^{(\eta)}$. In particular, the electron-gas approximation, Eq. (153), and the Colle-Salvetti functional, Eq. (151),

$$\overline{E}_{\text{co}}^{(\text{III})}[\gamma] \approx \mathcal{E}_{\text{co}}^{(\text{gas})}[\tau_g]_{(\tau_g=\gamma)}, \tag{190}$$

$$\overline{E}_{\text{co}}^{(\text{III})}[\gamma] \approx \mathcal{E}_{\text{co}}^{\text{cs}}[\tilde{\tau}_{\text{He}}]_{(\tilde{\tau}_{\text{He}}=\gamma)}. \tag{191}$$

Assuming both approximations are reasonable ones, we can use a linear combination of the two:

$$\overline{E}_{\text{co}}^{(\text{III})}[\gamma] \approx a_c\mathcal{E}_{\text{co}}^{\text{cs}}[\tilde{\tau}_{\text{He}}]_{(\tilde{\tau}_{\text{He}}=\gamma)} + (1-a_c)\mathcal{E}_{\text{co}}^{(\text{gas})}[\tau_g]_{(\tau_g=\gamma)}, \tag{192}$$

where a_c is an empirical parameter. This approximation is an alternative to the B3LYP functional [8,17] which uses analogous correlation-energy functionals: They use the LYP correlation-energy functional [18], derived from Colle-Salvetti one $\mathcal{E}_{\text{co}}^{\text{cs}}$, and a uniform-electron-gas functional, derived from the RPA [78]; they set $a_c=0.81$.

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APPENDIX A: PARTITIONING OF SECOND-QUANTIZED OPERATORS

We find it convenient to partition one-body operators, say $\hat{h}$,

$$\hat{h} = \sum_{ij} \hat{h}_{ij}, \tag{A1}$$

into the following four components:

$$\hat{h} = \hat{h}_{\text{ex}} + \hat{h}_{\text{de}} + \hat{h}_{\text{oc}} + \hat{h}_{\text{un}}, \tag{A2a}$$

where the excitation (ex), deexcitation (de), occupied (oc), and unoccupied (un) parts are given by the following expressions:

$$\hat{h}_{\text{ex}} = \sum_{wr} h_{rw} a_r^\dagger a_w, \tag{A2b}$$

$$\hat{h}_{\text{de}} = \sum_{wr} h_{wr} a_w^\dagger a_r, \tag{A2c}$$

$$\hat{h}_{\text{oc}} = \sum_{wx} h_{wx} a_w^\dagger a_x, \tag{A2d}$$

$$\hat{h}_{\text{un}} = \sum_{rs} h_{rs} a_r^\dagger a_s, \tag{A2e}$$

and the orbitals are defined with respect to a reference state $|\Phi\rangle$, as indicated by Eqs. (6).

Any second-quantized operator, say $\hat{O}$, can be partitioned into open and closed portions with respect to a single-reference or multireference space [54,79,80]. In our case, where the reference space is only spanned by a single-determinantal state, the closed portion of $\hat{O}$, say $\hat{O}_{\text{cl}}$, is simply a constant—as in Eqs. (17) and (18)—and is given by the fully contracted part of $\hat{O}$, where the operator is written in normal-ordered form with respect to the reference state $|\Phi\rangle$ [53,54,57,58]. Explicitly, we have

$$\hat{O}_{\text{cl}} = \hat{O}_0 = \langle\Phi|\hat{O}|\Phi\rangle, \tag{A3}$$

where the 0 subscript indicates the zero-body term.

The open portion of $\hat{O}$, say $\hat{O}_{\text{op}}$, is usually defined as the remaining portion; it is given by the one-, two- and higher-body terms, where, again, the operator is written in normal-ordered form. However, for our purposes, we use a more restrictive definition for $\hat{O}_{\text{op}}$, and define it by the necessary, or minimal, portion of $\hat{O}$ that is needed to satisfy the following condition:

$$\hat{O}_{\text{op}}|\Phi\rangle = Q_\Phi \hat{O}|\Phi\rangle. \tag{A4}$$

We define the remaining portion $\hat{O}_{\text{re}}$ by the following:

$$\hat{O} = \hat{O}_{\text{cl}} + \hat{O}_{\text{op}} + \hat{O}_{\text{re}}, \tag{A5}$$

so the following identities are satisfied;

$$(\hat{O}_{\text{cl}} + \hat{O}_{\text{op}})|\Phi\rangle = \hat{O}|\Phi\rangle, \tag{A6}$$

$$\hat{O}_{\text{re}}|\Phi\rangle = 0. \tag{A7}$$

The remaining portion $\hat{O}_{\text{re}}$ has at least one hole or particle annihilation operator. $\hat{O}_{\text{op}}$ has at least one pair of hole-particle creation operators and no hole or particle annihilation operators. In terms of diagrams, $\hat{O}_{\text{re}}$ has at least one external line below the vertex; $\hat{O}_{\text{op}}$ has no lines below the vertex and at least one pair of external lines above it; $\hat{O}_{\mathrm{cl}}$ has no external free lines.

Note that for a one-body operator, the open and excited portions are identical:

$$\hat{h}_{\mathrm{ex}} = \hat{h}_{\mathrm{op}}. \tag{A8}$$

APPENDIX B: ADDITIONAL RELATIONS FOR THE THIRD TRIAL WAVE FUNCTION

The operator product $H\hat{\Omega}_{\Phi}$ can be written as a sum of zero-, one-, two-, and higher-body excitations:

$$H\hat{\Omega}_{\Phi} = E_{\mathrm{III}}[\Phi] + (H\hat{\Omega}_{\Phi})_1 + (H\hat{\Omega}_{\Phi})_2 + (H\hat{\Omega}_{\Phi})_3 + \cdots, \tag{B1}$$

where we use the identity given by

$$E_{\mathrm{III}}[\Phi] = (H\hat{\Omega}_{\Phi})_{\mathrm{cl}} = (H\hat{\Omega}_{\Phi})_0, \tag{B2}$$

and this relation follow from Eqs. (59) and (80). (See also Appendix A.)

Substituting Eq. (B1) into Eq. (85) yields

$$(H\hat{\Omega}_{\Phi})_{\mathrm{op,cn}} - [(H\hat{\Omega}_{\Phi})_1]_{\mathrm{op,cn}} = 0. \tag{B3}$$

Using expansion (B1) again and noting that each term is linearly independent, we have

$$[(H\hat{\Omega}_{\Phi})_n]_{\mathrm{op,cn}} = 0, \quad n \geqslant 2. \tag{B4}$$

This relation can be used to obtain the coupled cluster equations for the $\hat{S}_n^{\Phi}$ amplitudes.

We now demonstrate that $|\Psi_{\Phi}^{(\mathrm{III})}\rangle$ is a valid trial wave function: Eq. (57) and the other relations from Sec. IV A are satisfied.

Consider a determinantal state, say $|\Theta'\rangle$, that we require to satisfy the following condition:

$$P_{11}^{\Theta'}(H\hat{\Omega}_{\Theta'})_{\mathrm{op,cn}} = 0. \tag{B5a}$$

Using Eq. (B1), we can easily verify that the following conditions causes Eq. (B5a) to be satisfied:

$$[(H\hat{\Omega}_{\Theta'})_1]_{\mathrm{op,cn}} = 0. \tag{B5b}$$

Adding Eqs. (B3) and (B5a), for ($|\Phi\rangle = |\Theta'\rangle$), and comparing the result with Eq. (28), indicates that

$$\hat{\Omega}_{\Theta'} = \Omega_{\Theta'}, \tag{B6}$$

and therefore we have

$$|\Psi_{\Theta'}^{(\mathrm{III})}\rangle = |\Psi\rangle. \tag{B7}$$

Multiplying Eq. (B7) by $P_{11}^{\Theta'}$ and using Eqs. (80), (81a), and (81b) gives

$$P_{11}^{\Theta'}|\Psi\rangle = 0. \tag{B8}$$

Comparing this equation with Eq. (48) indicate that $|\Theta'\rangle$ is the Brueckner state:

$$|\Theta'\rangle = |\Theta\rangle. \tag{B9}$$

Substituting this result into Eq. (B7) indicates that Eq. (57) is satisfies. All other relations from Sec. IV A are easily verified. For example, Eqs. (64)–(66) follow from Eq. (59) through Eq. (63).

Substituting Eq. (B9) into Eqs. (B5a) and (B5b) yields the following identities:

$$P_{11}^{\Theta}(H\hat{\Omega}_{\Theta})_{\mathrm{op,cn}} = 0, \tag{B10a}$$

$$[(H\hat{\Omega}_{\Theta})_1]_{\mathrm{op,cn}} = 0. \tag{B10b}$$

These equivalent relations are alternative representations of the Brillouin-Brueckner condition, since if they satisfied, then Eq. (58) is also satisfied. Note that $\hat{\Omega}_{\Phi}$ does not possess a single-excitation operator,. i.e., $\hat{S}_1^{\Phi}$ is absent in Eq. (81b).

Using the definition of an open operator, Eqs. (85) and (B10a) can be represented by the following:

$$\tilde{Q}_{\Phi}(H\hat{\Omega}_{\Phi})_{\mathrm{cn}}P_{\Phi} = 0, \tag{B11}$$

$$P_{11}^{\Theta}(H\hat{\Omega}_{\Theta})_{\mathrm{cn}}P_{\Theta} = 0, \tag{B12}$$

where

$$\tilde{Q}_{\Phi} = Q_{\Phi} - P_{11}^{\Phi}. \tag{B13}$$

Elsewhere [51] a general and transparent perturbative treatment of coupled cluster theory is presented that is also useful to obtain a perturbative expansion for the third correlation-energy functional $E_{\mathrm{co}}^{(\mathrm{III})}$.

APPENDIX C: ADDITIONAL RELATIONS FOR THE FOURTH TRIAL WAVE FUNCTION

The proof that Eqs. (57) and (64) are satisfied uses the Schrödinger equation (1), which can be written

$$P_{11}^{\Theta}H|\Psi\rangle + (1 - P_{11}^{\Theta})H|\Psi\rangle = \mathcal{E}P_{11}^{\Theta}|\Psi\rangle + \mathcal{E}(1 - P_{11}^{\Theta})|\Psi\rangle, \tag{C1}$$

where he have added, and also subtracted, P_{11}^{Θ} terms. Equations (44), (48), and (49) indicate that the first terms on the right and left sides vanish, so we have

$$(1 - P_{11}^{\Theta})H|\Psi\rangle = \mathcal{E}(1 - P_{11}^{\Theta})|\Psi\rangle. \tag{C2}$$

Equations (57) and (64), for $\eta = \mathrm{IV}$, are obtained by comparing Eqs. (86) and (C2), and using Eq. (56). All other relations from Sec. IV A are easily verified.

As in the exact wave function of interest $|\Psi\rangle$, the trial wavefunction $|\Psi_{\Phi}^{(\mathrm{IV})}\rangle$ can be generated by a wave operator $\tilde{\Omega}_{\Phi}$:

$$\tilde{\Omega}_{\Phi}|\Phi\rangle = |\Psi_{\Phi}^{(\mathrm{IV})}\rangle, \tag{C3}$$

where $\tilde{\Omega}_{\Phi}$ is similar to Ω_{Φ}—defined by Eqs. (42) and (43)—except that there is no excitation operator into P_{11}^{Φ}:

$$\tilde{\Omega}_{\Phi} = 1 + \tilde{\Omega}_2^{\Phi} + \tilde{\Omega}_3^{\Phi} + \cdots, \tag{C4}$$

where

$$\tilde{\Omega}_2^{\Phi} = \frac{1}{2!}\sum_{rwsx} \tilde{x}^{\Phi}_{rwsx} a_r^{\dagger} a_s^{\dagger} a_x a_w, \tag{C5a}$$

$$\tilde{\Omega}_3^{\Phi} = \frac{1}{3!}\sum_{rwsxty} \tilde{x}^{\Phi}_{rwsxty} a_r^{\dagger} a_s^{\dagger} a_t^{\dagger} a_y a_x a_w, \tag{C5b}$$

Using Eqs. (C3) and (C4), after substituting Eq. (61) into Eq. (60), gives the fourth correlation-energy functional

$$E_{\mathrm{co}}^{(\mathrm{IV})}[\Phi] = [H(\tilde{\Omega}_{\Phi} - 1)]_{\mathrm{cl}}, \tag{C6}$$

where we added

$$\langle \Phi | H P_{\Phi} (\tilde{\Omega}_{\Phi} - 1) | \Phi \rangle = 0. \tag{C7}$$

By using the definition of $\tilde{Q}_{\Phi}$, given by Eq. (B13), and by requiring H_0^{Φ} to satisfy

$$P_{11}^{\Phi} H_0^{\Phi} (1 - P_{11}^{\Phi}) = 0, \tag{C8}$$

it is easily proven that $\tilde{\Omega}_{\Phi}$ is a solution to the following variants of Eqs. (32) and (33):

$$\tilde{\Omega}_{\Phi} = 1 + \tilde{\Omega}_{\Phi}^{(1)} + \tilde{\Omega}_{\Phi}^{(2)} + \cdots, \tag{C9}$$

$$(E_0 - H_0^{\Phi}) \tilde{\Omega}_{\Phi}^{(n)} P_{\Phi} = \tilde{Q}_{\Phi} \left[V_{\Phi} \tilde{\Omega}_{\Phi}^{(n-1)} - \sum_{m=1}^{n-1} \tilde{\Omega}_{\Phi}^{(n-m)} \times P_{\Phi} V_{\Phi} \tilde{\Omega}_{\Phi}^{(m-1)} \right] P_{\Phi}. \tag{C10}$$

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