Developments for Reference–State One–Particle Density–Matrix Theory

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Abstract

Brueckner orbitals, and the density of the Brueckner reference-state, are shown to satisfy the same cusp condition – involving the nuclear charges – as natural- and Hartree–Fock-orbitals. Using the cusp condition, the density of a determinantal state can be used to determine the external potential, if the determinantal state is from either Hartee–Fock or Brueckner-orbital theory, as well as, determinant states obtained by many other formalisms that are defined by a one-body operator, if a portion of the one-body operator – the portion not associated with the kinetic energy or external potential – generates a well behaved function when acting on an occupied orbital. Using this relationship involving a determinant and its external potential, a variation of Reference–State One–Particle Density–Matrix Theory [arXiv:physics/0308056] is formulated, where the trial wavefunctions are universal, in the Kohn-Sham sense, since they do not depend on the external potential. The resulting correlation-energy functionals, are also, universal, except for a relatively small term involving the portion of the expectation value of the external potential with the trial wavefunctions that appears beyond the first order. The same approximate energy functionals that were shown to be valid for the previous $v$-dependent, Reference–State One–Particle Density–Matrix Theory [arXiv:physics/0308084], are shown to be valid for the current approach, except that the use of the LYP and Colle–Salvetti functional appear more natural within the current approach, since these functionals are universal ones. And since the BLYP and B3LYP functionals contain the LYP functional, these approaches are also better suited with the current approach.

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I. EXTERNAL POTENTIAL DETERMINED BY THE ONE-PARTICLE DEN-
SITY MATRIX AND THE PARTICLE DENSITY

There is a one-to-one correspondence between determinant states and their one-particle
density-matrices [1, 2]. Because of this correspondence, it is convenient to denote a deter-
minantal state that is determined by a one-particle density-matrix, say $\gamma$, simply by $|\gamma\rangle$. In
addition, any function, say $G$, that depends on $\gamma$, can be written as $G(\gamma)$; this same notation
also indicates that $G$ is determined by the corresponding determinant, $|\gamma\rangle$.

Consider the following noninteracting Hamiltonian:

$$ H_\gamma^s = \sum_{i} \left( -\frac{1}{2} \nabla^2 r_i + v(r_i) + \hat{w}_\gamma(x_i) \right), \quad (1) $$

where the external potential $v$ is given by a fixed set of point charges

$$ v(r) = -\sum_{m \in \{R_{\text{nuc}}\}} \frac{Z_m}{|R_m - r|}, \quad (2) $$

and the summation is over the coordinates of the nuclear point charges, denoted by $\{R_{\text{nuc}}\}$; furthermore, $\hat{w}_\gamma$ may be non-local and this operator can depend on the spin-coordinate $\omega$, where the spatial and spin coordinates are denoted collectively by $x$; in addition, the $\gamma$ superscript appended to $w$ indicates that this operator may also depend on $\gamma$ (or equivalently $|\gamma\rangle$).

Consider a determinantal state, say $|\gamma\rangle$, that satisfies the Schrödinger Eq:

$$ H_\gamma^s |\gamma\rangle = E_\gamma |\gamma\rangle, \quad (3) $$

where the Hamiltonian $H_\gamma^s$ is given by Eq. (1); furthermore, the noninteracting eigenstate,$|\gamma\rangle$, can be expressed by a unique set of occupied orbitals, denoted by $\{\psi_o \leftarrow \gamma, \hat{f}_\gamma\}$; each of these orbitals satisfy the following one-particle Schrödinger Eq:

$$ \hat{f}_\gamma \psi_{\sigma \sigma}^\gamma(x) = \tilde{\epsilon}_{\sigma} \psi_{\sigma \sigma}^\gamma(x), \quad \sigma = \alpha, \beta, \quad \psi_{\sigma \sigma}^\gamma \in \{\psi_o \leftarrow \gamma, \hat{f}_\gamma\}, \quad (4) $$

where the one-body operator is given by

$$ \hat{f}_\gamma = -\frac{1}{2} \nabla^2 r + v(r) + w_\gamma(x). \quad (5) $$

In addition, we require the operator $w_\gamma$ to be Hermitian and satisfy

$$ \lim_{|R - r| \to 0} |R - r| w_\gamma(r, \omega) \psi_{\sigma \sigma}^\gamma(r, \omega) = 0, \quad \text{for all } R. \quad (6) $$
In order to emphasize an exclusive dependence upon \( R \), we modify the limit in this Eq., giving

\[
\lim_{r \to R} |r - R| w^\gamma(r, \omega) \psi_{x\sigma}^\gamma(r, \omega) = 0. \quad \text{for all } R.
\]

(7)

Let us also mention that the set of unoccupied orbitals – orthogonal to \{\psi_o \leftarrow \gamma, \hat{f}_\gamma\} – is denoted by \{\psi_u \leftarrow \gamma, \hat{f}_\gamma\} and, in addition, all of our spin-orbitals \( \psi_{i\sigma}(x) \) have the following form:

\[
\psi_{i\sigma}(x) = \chi_{i\sigma}(r) \sigma(\omega), \quad \sigma = \alpha \text{ or } \beta,
\]

(8)

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

Multiplying Eq. (4) by \(|r - R|\) followed by taking a limit of this term vanishing, gives

\[
\lim_{|r - R| \to 0} |r - R| \left( -\frac{1}{2} \nabla_r^2 - \sum_{m \in \{R_{\text{nuc}}\}} \frac{Z_m}{|R_m - r|} \right) \psi_{x\sigma}^\gamma(x) = 0,
\]

(9)

where we have used Eqs. (2), (5), and (6). (Note that this Eq. is also the cusp condition \[3, 4\], however, in that case, \( \psi_{x\sigma}^\gamma \) is a natural orbital and \( \gamma \) is the one-particle density-matrix of an interacting target-state, say \( \Psi \).)

In order to obtain an exclusive dependence upon \( R \), we, again, modify the limit in this Eq, giving

\[
\lim_{r \to R} |r - R| \left( -\frac{1}{2} \nabla_r^2 - \sum_{m \in \{R_{\text{nuc}}\}} \frac{Z_m}{|R_m - r|} \right) \psi_{x\sigma}^\gamma(x) = 0.
\]

(10)

Since the second term vanishes unless \( R \in \{R_{\text{nuc}}\} \), we have

\[
\lim_{r \to R} |r - R| \left( -\frac{1}{2} \nabla_r^2 - \sum_{m \in \{R_{\text{nuc}}\}} \delta_{RR_m} Z_m \right) \psi_{x\sigma}^\gamma(x) = 0,
\]

(11)

which can be written as

\[
\lim_{r \to R} |r - R| \psi_{x\sigma}^\gamma(x)^{-1} \left( -\frac{1}{2} \nabla_r^2 \right) \psi_{x\sigma}^\gamma(x) = \sum_{m \in \{R_{\text{nuc}}\}} \delta_{RR_m} Z_m.
\]

(12)

Defining the left side by

\[
T(\psi_{x\sigma}^\gamma, R) = \lim_{r \to R} |r - R| \psi_{x\sigma}^\gamma(x)^{-1} \left( -\frac{1}{2} \nabla_r^2 \right) \psi_{x\sigma}^\gamma(x),
\]

(13)
we can write
\[ T(\psi_x^\gamma, \mathbf{R}) = \sum_{m \in \{\mathbf{R}_{\text{nuc}}\}} \delta_{\mathbf{R} \mathbf{R}} Z_m. \] (14)

For a set of spatially restricted orbitals:
\[ \psi_x^\gamma(x) = \chi_x^\gamma(r) \sigma(\omega), \] (15)

it is readily proven that we have
\[ T(\chi_x^\gamma, \mathbf{R}) = \sum_{m \in \{\mathbf{R}_{\text{nuc}}\}} \delta_{\mathbf{R} \mathbf{R}} Z_m. \] (16)

Multiplying Eq. (11) by \( (\psi_x^\gamma(x'))^* \), and summing over all occupied orbitals from the set \( \{\psi_o \leftarrow \gamma, \hat{f}_\gamma\} \), gives
\[ \lim_{r \to \mathbf{R}} |r - \mathbf{R}| \left( -\frac{1}{2} \nabla_r^2 \right) \gamma(x, x') = 0, \] (17)

where the one-particle density matrix is given by
\[ \gamma(x, x') = \sum_{x\sigma \in \{\psi_o \leftarrow \gamma, \hat{f}_\gamma\}} \psi_x^\gamma(x) (\psi_x^\gamma(x'))^* \] (18)

and it is readily proven that we have
\[ T(\gamma, \mathbf{R}) = \sum_{m \in \{\mathbf{R}_{\text{nuc}}\}} \delta_{\mathbf{R} \mathbf{R}} Z_m, \] (19)

where
\[ T(\gamma, \mathbf{R}) = \lim_{r \to \mathbf{R}} |r - \mathbf{R}| \gamma(x, x')^{-1} \left( -\frac{1}{2} \nabla_r^2 \right) \gamma(x, x'). \] (20)

Since this expression is invariant to the variable \( x' \), we can choose \( x' = x \), yielding
\[ T(\gamma, \mathbf{R}) = \lim_{r \to \mathbf{R}} |r - \mathbf{R}| \gamma(x, x)^{-1} \left( -\frac{1}{2} \nabla_r^2 \right) \gamma(x, x'). \] (21)

Since Eq. (11) is also satisfied by the complex conjugate orbital, \( \psi_x^\gamma(x)^* \), it is readily shown that we have
\[ T(\gamma^*, \mathbf{R}) = \sum_{m \in \{\mathbf{R}_{\text{nuc}}\}} \delta_{\mathbf{R} \mathbf{R}} Z_m, \] (22)
where

\[ T(\gamma, R) = \lim_{r \to R} |r - R|^{-1} \left( \left(-\frac{1}{2} \nabla_r^2 \right) \gamma(x, x') \right)_{x'=x}. \]  

(23)

Adding together Eq. (19) and (22), using (21) and (23), and using the following identity:

\[ \left(-\frac{1}{2} \nabla_r^2 \right) \gamma(x, x) = \left(\left(-\frac{1}{2} \nabla_r^2 \right) \gamma(x, x') \right)_{x'=x} + \left(\left(-\frac{1}{2} \nabla_r^2 \right) \gamma(x', x) \right)_{x'=x}, \]  

(24)

we get

\[ T(\rho_s, R) = 2 \sum_{m \in \mathbb{R}_{\text{nuc}}} \delta_{RR_m} Z_m, \]  

(25)

where

\[ T(\rho_s, R) = \lim_{r \to R} |r - R|^{-1} \left(-\frac{1}{2} \nabla_r^2 \right) \rho_s(x), \]  

(26)

and \( \rho_s(x) \) is the spin density, i.e.,

\[ \rho_s(x) = \gamma(x, x). \]  

(27)

Eq. (17) is also valid for \( \gamma(r, \omega; r', \omega) \) replacing \( \gamma(x, x') \); making this substitution and summing over the spin-variable \( \omega \) we obtain the same expression, as Eq. (17), except that it involves the spinless density matrix \( \rho_1 \), given by

\[ \rho_1(r, r') = \sum_\omega \gamma(r, \omega; r', \omega), \]  

(28)

and it is readily proven that we have

\[ T(\rho_1, R) = \frac{1}{2} T(\rho, R) = \sum_{m \in \mathbb{R}_{\text{nuc}}} \delta_{RR_m} Z_m, \]  

(29)

where \( T(\rho_1, R) \) and \( T(\rho, R) \) are defined by Eqs. (21) and (26), respectively; \( \rho \) is the electron density, i.e.,

\[ \rho(r) = \rho_1(r, r). \]  

(30)

Consider the set of (ground and excited) determinantal states, denoted \( \{ |\gamma\rangle_v \} \), that are eigenfunctions of \( H_s \), given by Eq. (1), where the states from the set, \( \{ |\gamma\rangle_v \} \), are obtained from all \( w^* \) that satisfy Eq. (7), and from all Coulombic external-potentials \( v \), given by Eq. (2). From the density of any one of theses states, say \( \rho \), we can determine its Coulombic external-potential \( v \) by using Eqs. (29) and (2). Hence, \( v \) is a unique function of the density. In other words, we have \( v(\rho) \), and this function is defined for all densities that are from this set of determinantal states, \( \{ |\gamma\rangle_v \} \).
II. INVARIANCE OF OCCUPIED-ORBITAL TRANSFORMATION

We now partition the operator $w^\gamma$ into the following four components:

$$w^\gamma = w^\gamma_{\text{ex}} + w^\gamma_{\text{de}} + w^\gamma_{\text{oc}} + w^\gamma_{\text{un}},$$  \hspace{1cm} (31)

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

$$w^\gamma_{\text{ex}} = \sum_{w\sigma r\sigma'} w^\gamma_{w\sigma r\sigma'} a_{r\sigma}^{\dagger} a_{w\sigma'},$$  \hspace{1cm} (32)

$$w^\gamma_{\text{de}} = \sum_{r\sigma w\sigma'} w^\gamma_{w\sigma r\sigma'} a_{w\sigma}^{\dagger} a_{r\sigma'},$$  \hspace{1cm} (33)

$$w^\gamma_{\text{oc}} = \sum_{w\sigma x\sigma'} w^\gamma_{w\sigma x\sigma'} a_{w\sigma}^{\dagger} a_{x\sigma'},$$  \hspace{1cm} (34)

$$w^\gamma_{\text{un}} = \sum_{r\sigma s\sigma'} w^\gamma_{r\sigma s\sigma'} a_{r\sigma}^{\dagger} a_{s\sigma'},$$  \hspace{1cm} (35)

and the occupied- and unoccupied-orbitals are, respectively, given by

$$\psi^\gamma_{w\sigma}, \psi^\gamma_{x\sigma} \in \{\psi_{\omega} \leftarrow \gamma, \hat{f}_\gamma \},$$  \hspace{1cm} (36)

$$\psi^\gamma_{r\sigma}, \psi^\gamma_{s\sigma} \in \{\psi_{\omega} \leftarrow \gamma, \hat{f}_\gamma \}. $$  \hspace{1cm} (37)

The results from the previous Sec. indicate that $v$ is a function of $\rho$ for any $\rho$ determined from $H_{\gamma}^\gamma$, given by Eq. (1) – or, equivalently, any $\rho$ determined from the one-body operator $\hat{f}_\gamma$ given by (5) – when the operator $w^\gamma$ satisfies Eq. (7). Using the partitioning method given above, Eq. (7) becomes

$$\lim_{|r-R| \to 0} |r-R| [w^\gamma_{\text{oc}}(r,\omega) + w^\gamma_{\text{ex}}(r,\omega)] \psi^\gamma_{w\sigma}(r,\omega) = 0, \text{ for all } R,$$  \hspace{1cm} (38)

indicating that Eq. (7) can be satisfied with any choice of $w^\gamma_{\text{de}}$ and $w^\gamma_{\text{un}}$.

The above relation is satisfied when we have

$$\lim_{r \to R} |r-R| w^\gamma_{\text{oc}}(r,\omega) \psi^\gamma_{w\sigma}(r,\omega) = 0,$$  \hspace{1cm} (39a)

$$\lim_{r \to R} |r-R| w^\gamma_{\text{ex}}(r,\omega) \psi^\gamma_{w\sigma}(r,\omega) = 0.$$  \hspace{1cm} (39b)

It is easily proven that a determinantal state $|\gamma\rangle$ that satisfies Eq. (3) – and the corresponding density $\rho$ from $|\gamma\rangle$ – does not depend on $w^\gamma_{\text{oc}}$; so, when considering the statements appearing in the last paragraph of the previous section, we can relax the requirement that
Eq. (7) be satisfied, and only require Eq. (39b) to be satisfied. In other words, the density of a determinantal state, that satisfies Eq. (3), can be used to determine its external potential, given by Eq. (2), by using Eq. (29), if (39b) is satisfied. An equivalent statement refers to the one-body operator $\hat{f}_\gamma$: The density of a determinantal state can be used to determine its external potential, given by Eq. (2), by using Eq. (29), if (39b) is satisfied, where the orbitals defining the determinantal state $|\gamma\rangle$ are the occupied eigenfunctions of $\hat{f}_\gamma$, defined by Eq. (5). Note that the $w_{\text{oc}}^\gamma$ and $w_{\text{un}}^\gamma$ portions of the operator $w^\gamma$ are at our disposal, since the determinantal state does not depend on these components; $w_{\text{de}}^\gamma$ is determined by $w_{\text{ex}}^\gamma$, since $w^\gamma$ is required to be Hermitian. (The Hermitian requirement can be dropped by using a biorthogonal basis set.)

III. HARTREE–FOCK DETERMINANTAL STATES

We now show that the set of Hartree–Fock determinantal states, say $\{|\tilde{\tau}\rangle\}$, are members of $\{|\gamma\rangle_{\nu}\}$, indicating that their Coulombic external-potentials $v$ can be uniquely determined by their electron density, i.e., $v(\rho)$, by using Eq. (29).

The occupied, canonical Hartree–Fock orbitals satisfy the following single particle Eq:

$$\hat{F}_\tau \psi^\rho_{x\sigma}(x) = \epsilon^\rho_{x\sigma} \psi^\rho_{x\sigma}(x), \quad \sigma = \alpha, \beta, \quad \psi^\rho_{x\sigma} \in \{\psi_0 \leftarrow \tilde{\tau}, \hat{F}_\tau\}$$

(40)

where the Fock operator is given by

$$\hat{F}_\tau = -\frac{1}{2} \nabla^2_r + v(r) + \int r_{12}^{-1} \tau(x_2, x_2) \, dx_2 + \hat{v}_x^\tau(x),$$

(41)

and the one-particle density-matrix for the Hartree–Fock reference-state has the following form:

$$\tilde{\tau}(x, x') = \sum_{x\sigma \in \{\psi_0 \leftarrow \tilde{\tau}, \hat{F}_\tau\}} \psi^\rho_{x\sigma}(x) (\psi^{\rho*}_{x\sigma}(x'))^*;$$

(42)

Furthermore, the exchange operator, $\hat{v}_x^\tau$, is a non-local operator that is defined by its kernel, $-r_{12}^{-1}\gamma$. Therefore, for an arbitrary function, say $\psi$, we have

$$\hat{v}_x^\tau(x_1)\psi(x_1) = -\int dx_2 \, r_{12}^{-1} \tau(x_1, x_2) \psi(x_2).$$

(43)

Equating Eqs. (40) and (41) with (4) and (5), for ($\gamma = \tilde{\tau}$), we have

$$w^\gamma(x) = \int r_{12}^{-1} \tau(x_2, x_2) \, dx_2 + \hat{v}_x^\gamma(x),$$

(44)
and it is easily seen that Eq. (7) is satisfied; so, the Hartree–Fock states are members of \( \{ | \gamma \rangle_v \} \), and we have \( v(\tilde{\rho}) \) where \( \tilde{\rho} \) is the Hartree–Fock density:

\[
\tilde{\rho}(r) = \sum_\omega \tilde{\tau}(r, \omega; r, \omega).
\]  

(45)

The Hartree–Fock Eqs. are usually solved using an iterative, self consistent field (SCF) approach, where the \((m-1)\)th iteration is given by

\[
\hat{F}_{\tau_{m-1}} \psi_{x\sigma}^{\tau_m}(x) = \epsilon_{x\sigma}^{\tau_m} \psi_{x\sigma}^{\tau_m}(x), \quad \sigma = \alpha, \beta, \quad \psi_{x\sigma}^{\tau_m} \in \{ \psi_\alpha \leftarrow \tilde{\tau}, \hat{F}_{\tau_{m-1}} \} 
\]  

(46)

and its easily seen that Eq. (7) is satisfied for \( w^{\tau_{m-1}} \), so all determinantal states determined during the SCF approach are also members of \( \{ | \gamma \rangle_v \} \).

Consider another Hermitian Fock-type operator, say \( \hat{F}'_{\gamma} \), that is given by

\[
\hat{F}'_{\gamma} = \hat{F}_{\gamma} + \hat{v}_{x+}^{\gamma}
\]  

(47)

where the excitation (ex) portion of the additional exchange-operator \( \hat{v}_{x+}^{\gamma} \) is zero:

\[
(\hat{v}_{x+}^{\gamma})_{ex} = 0.
\]  

(48)

Hence, according to Sec. 11 Eq. (39b) remains satisfied and, in addition, the determinantal state defined by the occupied orbitals, from \( \hat{F}'_{\gamma} \), is the same the determinantal state from \( \hat{F}_{\gamma} \); it is a member of \( \{ | \gamma \rangle_v \} \); so, again, the density of this determinantal state can be used to determine the external potential \( v \), Eq. (2), by using Eq. (29). Furthermore, since the occupied eigenfunctions from \( \hat{F}'_{\gamma} \), given by

\[
\hat{F}'_{\gamma} \psi_{x\sigma}^{\gamma}(x) = \epsilon_{x\sigma}^{\gamma} \psi_{x\sigma}^{\gamma}(x), \quad \sigma = \alpha, \beta, \quad \psi_{x\sigma}^{\gamma} \in \{ \psi_\alpha \leftarrow \tilde{\tau}, \hat{F}'_{\gamma} \}
\]  

(49)

differ only by a unitary transformation from the \( \hat{F}_{\gamma} \) occupied orbitals, \( \{ \psi_\alpha \leftarrow \tilde{\tau}, \hat{F}_{\gamma} \} \). Therefore, and of course, the one-particle density-matrix obtained from these occupied orbitals are equivalent:

\[
\tilde{\tau}(x, x') = \sum_{x\sigma \in \{ \psi_\alpha \leftarrow \tilde{\tau}, \hat{F}'_{\gamma} \}} \psi_{x\sigma}^{\gamma}(x) (\psi_{x\sigma}^{\gamma}(x'))^*,
\]  

(50)

where this one-particle density-matrix \( \tilde{\tau} \) is the same one appearing in Eq. (12).
IV. GENERALIZED FOCK OPERATOR

Consider a generalized Fock-operator \( \hat{F}_\gamma \), where its occupied orbitals satisfy

\[
\hat{F}_\gamma \psi_\gamma^\sigma(x) = \varepsilon^\gamma_\sigma \psi_\gamma^\sigma(x), \quad \sigma = \alpha, \beta, \quad \psi_\gamma^\sigma \in \{ \psi_0 \leftarrow \gamma, \hat{F}_\gamma \}
\]

and \( \hat{F}_\gamma \) is given by

\[
\hat{F}_\gamma = -\frac{1}{2} \nabla^2 + v(r) + \int r_{12}^{-1} \gamma(x_2, x_2) \, dx_2 + \hat{v}_x^\gamma(x) + \hat{v}_co^\gamma(x).
\]

Comparing the above two Eqs. with (4) and (5), we obtain a new definition for \( w^\gamma : \)

\[
w^\gamma(x) = \int r_{12}^{-1} \gamma(x_2, x_2) \, dx_2 + \hat{v}_x^\gamma(x) + \hat{v}_co^\gamma(x).
\]

and substituting this expression into Eq. (39b), gives

\[
\lim_{r \to R} |r - R| [\hat{v}_co^\gamma(r, \omega)]_{ex} \psi_\omega^\gamma(r, \omega) = 0, \quad \text{for all } R.
\]

Hence, if this relation is satisfied, the determinantal state defined by the occupied orbitals, from \( \hat{F}_\gamma \), is a member of \( \{ | \gamma \rangle_v \} \); so, again, the density of this determinantal state can be used to determine the external potential \( v \), Eq. (2), by using Eq. (29).

V. BRUECKNER DETERMINANTAL STATES

We seek solutions of the time-independent Schrödinger equation,

\[
H_v |\Psi\rangle = \mathcal{E} |\Psi\rangle,
\]

where \( H_v \) denotes the Hamiltonian operator defined by the external potential \( v \), where the Hamiltonian is independent of the number of electrons when it is expressed in second quantization:

\[
H_v = \sum_{i\sigma j\sigma} (i\sigma |\hat{h}| j\sigma) a^\dagger_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{i\sigma j\sigma k\sigma l\sigma'} (i\sigma j\sigma |k\sigma' l\sigma') a^\dagger_{i\sigma} a^\dagger_{k\sigma'} a_{l\sigma'} a_{j\sigma}
\]

where our Hamiltonian is spin-free; the spin-free integrals are written using chemist’s notation \([5]\):

\[
(i\sigma |\hat{h}| j\sigma) = \int \chi^*_i(r) (-\frac{1}{2} \nabla^2 + v(r)) \chi_j(r) \, dr,
\]

\[
(i\sigma j\sigma |k\sigma' l\sigma') = \int \chi^*_i(r_1) \chi_j(r_1) r_{12}^{-1} \chi^*_k(r_2) \chi_{l\sigma'}(r_2) \, dr_1 \, dr_2,
\]
and the creation and annihilation operators, $a_{i\sigma}^{\dagger}$ and $a_{i\sigma}$, correspond to the unrestricted spin-orbitals, $\psi_{i\sigma}$, defined by Eq. (8).

The wavefunction of interest $|\Psi\rangle$ can be generated by a wave operator $\Omega_{\gamma}$:

$$\Omega_{\gamma}|\gamma\rangle = (1 + \chi_{\gamma})|\gamma\rangle = |\Psi\rangle,$$

and the second relation defines the correlation operator, $\chi_{\gamma}$; furthermore, $|\gamma\rangle$ is any determinantal reference-state that overlaps with the target state: $\langle \gamma | \Psi \rangle \neq 0$.

Brueckner orbital theory is a generalization of Hartree–Fock theory that utilizes a single-determinantal state that has the maximum overlap with the target state. By definition, if $|\tau\rangle$ is a Brueckner reference-state, then the target state, $|\Psi\rangle$, contains no singly-excited states from $|\tau\rangle$:

$$\langle \tau | r_{\sigma} w_{\sigma}' | \Psi \rangle = 0,$$

and the singly-excited states are given by

$$|\tau_{w_{\sigma}} r_{\sigma}' \rangle = a_{r_{\sigma}'}^{\dagger} a_{w_{\sigma}} |\tau\rangle,$$

where the Brueckner-state occupied- and unoccupied-orbitals are, respectively, given by

$$\psi_{u_{\sigma}}^{r_{\sigma}}, \psi_{x_{\sigma}}^{r_{\sigma}} \in \{\psi_{o} \rightarrow \tau\},$$

and this notation indicates that the occupied orbitals determine $\tau$; furthermore, the unoccupied orbitals also determine $\tau$ since the union of the two orthogonal sets (of orbitals) is a complete set.

Note that, unlike the orbitals that are defined by Eq. (36), the occupied orbitals that satisfy Eq. (62) are not completely defined; they are invariant to a unitary transformation; similarly, the unoccupied orbitals that satisfy Eq. (63) are also invariant to a unitary transformation. Using a set of these orbitals, the Brueckner one-particle density-matrix is given by

$$\tau(x, x') = \sum_{x_{\sigma} \in \psi_{o} \rightarrow \tau} \psi_{x_{\sigma}}^{r_{\sigma}}(x) (\psi_{x_{\sigma}}^{r_{\sigma}}(x'))^*,$$

(64)
and, for future use, we mention that the virtual orbitals define the following two-body function:

$$\kappa_\tau(x, x') = \sum_{r\sigma \in \{\psi_{u\to\tau}\}} \psi_\tau^r(x) (\psi_\tau^r(x'))^*, \quad (65)$$

where, for a complete set of one-particle functions, the sum of the two gives the Dirac delta function:

$$\delta(x, x') = \kappa_\tau(x, x') + \tau(x, x'). \quad (66)$$

Since our Hamiltonian, given by Eq. (56), is spin-free, it is easily demonstrated that we have

$$\langle \gamma^r_{\sigma'} | \Psi \rangle = 0, \quad \text{for } \sigma \neq \sigma' \text{ and } \langle \gamma | \Psi \rangle \neq 0; \quad (67)$$

hence, we can modify the definition for a Brueckner reference-state, given by Eq. (60), and only consider the spin-conserving matrix-elements:

$$\langle \tau^r_{\sigma} | \Psi \rangle = 0. \quad (68)$$

Because of spin symmetry, Eq. (67) certainly holds when $|\gamma\rangle$ is a determinantal state that is an eigenfunction of the total spin angular-momentum operator, $\hat{S}_z^2$, e.g., a closed-shell ground-states with spatially restricted spin orbitals. However, this identity should also hold in more general cases, since, diagrammatically speaking, the spin state – either $\alpha$ or $\beta$ – must be conserved along an oriented path [24], and $w\sigma$ and $r\sigma'$ are on the same oriented path. In order to simplify our discussions, henceforth, we only consider cases where Eq. (67) holds; however, the result are easily generalized to the more general case, e.g., when the Hamiltonian is spin-dependent.

Substituting Eqs. (55) and (59) into (68), sequentially, we obtain

$$0 = \langle \tau^r_{\sigma} | \Psi \rangle = \langle \tau^r_{\sigma} | H_v | \Psi \rangle = \langle \tau^r_{\sigma} | H_v \Omega_\tau | \tau \rangle = \langle \tau^r_{\sigma} | H_v | \tau \rangle + \langle \tau^r_{\sigma} | H_v \chi_\tau | \tau \rangle, \quad (69)$$

and the vanishing of the above matrix elements involving $H_v$ is know as the Brillouin–Brueckner condition [7, 9, 22, 25, 26]. Writing the operator-product $H_v \chi_\tau$ in normal-ordered form [24, 27, 28, 29] with respect to the reference state $|\tau\rangle$, the last matrix element of the above Eq. becomes

$$\langle \tau^r_{\sigma} | H_v \chi_\tau | \tau \rangle = \langle \tau^r_{\sigma} | (H_v \chi_\tau)_1 | \tau \rangle, \quad (70)$$
where the one-body portion, \((H_v \chi_\tau)_1\), can be partitioned in the following manner:

\[
(H_v \chi_\tau)_1 = [(H_v \chi_\tau)_1]_{\text{op}} + [(H_v \chi_\tau)_1]_{\text{re}},
\]

(71)

and where the open (op) portion and remaining (re) portions have the following explicit forms:

\[
[(H_v \chi_\tau)_1]_{\text{op}} = \sum_{w\sigma r\sigma} U_{w\sigma r\sigma}^{\tau} a_{r\sigma}^{\dagger} a_{w\sigma},
\]

(72)

\[
[(H_v \chi_\tau)_1]_{\text{re}} = \sum_{r\sigma w\sigma} U_{r\sigma w\sigma}^{\tau} a_{r\sigma}^{\dagger} a_{w\sigma} + \sum_{r\sigma s\sigma} U_{r\sigma s\sigma}^{\tau} a_{w\sigma}^{\dagger} a_{r\sigma} - \sum_{w\sigma x\sigma} U_{w\sigma x\sigma}^{\tau} a_{w\sigma} a_{x\sigma}^{\dagger};
\]

(73)

furthermore, the one-body matrix-elements are defined by

\[
U_{i\sigma}^{j\sigma} = \langle \psi_\tau^{j\sigma} | (H_v \chi_\tau)_1 | \psi_\tau^{i\sigma} \rangle,
\]

(74)

and the orbital indices are given by the right side of Eqs. (32) and (33); this choice is indicated by the \(\tau\) superscripts appended to the summations, i.e., \(\sum_{\tau}\). (Note that the definition of an open operator given above differs from the definition used by other authors [29, 32, 33].)

In the above matrix elements, the ones that do not preserve the spin, i.e., \((U_{i\sigma}^{j\sigma'})\) for \(\sigma \neq \sigma'\), are omitted, since they can easily be shown to vanish for a spin-free Hamiltonian. (The vanishing of these matrix elements occurs, diagrammatically speaking, since the spin state – either \(\alpha\) or \(\beta\) – must be conserved along an oriented path [24], and \(i\sigma\) and \(j\sigma'\) are on the same oriented path.)

Substituting Eq. (71) into (70) and using (72) and (73), gives

\[
\langle \tau_{w\sigma}^{r\sigma} | (H_v \chi_\tau)_1 | \tau \rangle = \langle \tau_{w\sigma}^{r\sigma} | [(H_v \chi_\tau)_1]_{\text{op}} | \tau \rangle.
\]

(75)

Since the one-body operator-product \([(H_v \chi_\tau)_1]_{\text{op}}\) can also act within the one-body sector of the Hilbert space, we have the following identity:

\[
\langle \tau_{w\sigma}^{r\sigma} | [(H_v \chi_\tau)_1]_{\text{op}} | \tau \rangle = \langle \psi_{r\sigma}^{r\sigma} | [(H_v \chi_\tau)_1]_{\text{op}} | \psi_{w\sigma}^{r\sigma} \rangle.
\]

(76)

Substituting Eq. (70) into the Brillouin–Brueckner condition, Eq. (69), and using Eq. (75) and (76), and also the following identity:

\[
\langle \psi_{r\sigma}^{r\sigma} | (\hat{F}_\tau)_{\text{ex}} | \psi_{w\sigma}^{r\sigma} \rangle = \langle \tau_{w\sigma}^{r\sigma} | H_v | \Psi \rangle,
\]

(77)
involving the Fock operator, Eq. (11), yields

\[ \langle \psi^r_{\tau\sigma} | (F^r_\tau)^{\text{ex}} | \psi^r_{w\sigma} \rangle + \langle \psi^r_{\tau\sigma} | (\hat{v}^r_{\tau\sigma})^{\text{ex}} | \psi^r_{w\sigma} \rangle = 0, \]  

(78)

where the introduced correlation potential $\hat{v}^r_{\tau\sigma}$, by definition, satisfies

\[ (\hat{v}^r_{\tau\sigma})^{\text{ex}} = \left[ (H_v \chi_{\tau})^1 \right]_{\text{op}}, \]  

(79)

and the operators, $(F^r_\tau)^{\text{ex}}$ and $(\hat{v}^r_{\tau\sigma})^{\text{ex}}$, are defined in an analogous way as $w^{\gamma}_{\text{ex}}$, as indicated by Eqs. (31) through (35).

Since the above form of the Brillouin–Brueckner condition, given by Eq. (78), is satisfied by all pairs of orbitals involving one unoccupied-orbital and one occupied-orbital, we have

\[ (F^r_\tau)^{\text{ex}} = 0, \]  

(80)

where the generalized, or exact, Fock operator is defined by

\[ \hat{F}^r_\tau = F^r_\tau + \hat{v}^r_{\tau\sigma}. \]  

(81)

Comparing this definition of $\hat{F}^r_\tau$ with the one given by Sec. IV, Eq. (52), and using Eq. (41), we see that, for $(\gamma = \tau)$, the two definitions are equivalent, except that in this Sec. we require the excitation (ex) portion of the correlation potential $\hat{v}^r_{\tau\sigma}$ to satisfy Eq. (79); by arbitrarily defining the other portions of $\hat{v}^r_{\tau\sigma}$ we can diagonalize $\hat{F}^r_\tau$, and this eigenvalue Eq. is given by Eq. (51) for $(\gamma = \tau)$:

\[ \hat{F}^r_\tau \psi^r_{\xi\sigma}(x) = \varepsilon^r_{\xi\sigma} \psi^r_{\xi\sigma}(x), \quad \sigma = \alpha, \beta, \quad \psi^r_{\xi\sigma} \in \{ \psi \leftarrow \tau, F^r_\tau \}, \]  

(82)

and, furthermore, Eq. (54) becomes

\[ \lim_{r \to R} |r - R| \left[ \hat{v}^r_{\tau\sigma}(r, \omega) \right]_{\text{ex}} \psi^r_{w\sigma}(r, \omega) = 0, \quad \text{for all } R, \]  

(83)

where $(\hat{v}^r_{\tau\sigma})^{\text{ex}}$ is given by Eq. (79). Hence, if this relation is satisfied, Bruckner determinantal states $\{|\tau\rangle\}$ are member of $\{|\gamma\rangle_v\}$; so, again, the density of a Bruckner determinantal state can be used to determine its external potential $v$, Eq. (2), by using Eq. (29).

Using the results from appendix (B), we have

\[ \lim_{r_1 \to R} |r_1 - R| \left[ \hat{v}^r_{\tau\sigma}(x_1) \right]_{\text{ex}} \psi^r_{w\sigma}(x_1) = \lim_{r_1 \to R} |r_1 - R| \left( C^{x\sigma}_{w\sigma} \hat{h}_{v1} \psi^r_{x\sigma}(x_1) + D^{x\sigma}_{w\sigma} \hat{h}_{v1} \psi^r_{r\sigma}(x_1) \right), \]  

(84)
where
\[ \hat{h}_{v_1} = -\frac{1}{2} \nabla^2_{r_1} + v(r_1), \] (85)
and there are summations over the repeated indices \( x_\sigma \) and \( r_\sigma \) for the orbital sets \( \{ \psi_o \leftrightarrow \tau, \hat{F}_\tau \} \) and \( \{ \psi_u \leftrightarrow \tau, \hat{F}_\tau \} \). (The coefficients \( C^{x_\sigma}_{w_\sigma} \) and \( D^{r_\sigma}_{w_\sigma} \) are defined by Eqs. (B38) and (B39).)

Unfortunately we have been unable to prove that Eq. (83) is an identity by using Eq. (84). So, as an alternative approach, consider the case where the above identity, given by Eq. (83), is not necessarily satisfied. As in the derivation Eq. (9), by multiplying Eq. (82) by \(|r_1 - R|\) followed by taking a limit of this term vanishing, gives the following identity that must be satisfied:
\[ \lim_{r_1 \to R} |R - r_1| \hat{h}_{v_1} \psi_{w_\sigma}^{r}(x_1) + \lim_{r_1 \to R} |R - r_1| [\hat{v}_{co}^r(r_1, \omega)]_{ex} \psi_{w_\sigma}^{r}(r_1, \omega) = 0, \] (86)
where we have used Eqs. (81), (85), and (41) and, also, omitted the Coulomb and exchange terms, since these terms vanish; furthermore, we have used the decomposition of \( \hat{v}_{co}^r \) as defined by Eq. (31), and have chosen \((\hat{v}_{co}^r)_{oc}\) to be zero, since, according to the discussion within Sec. II, this portion is at our disposal; the one-particle density-matrix \( \tau \) is invariant to this choice.

Substituting Eq. (84) into (86), gives
\[ \lim_{r_1 \to R} |R - r_1| \hat{h}_{v_1} \psi_{x_\sigma}^{r}(x) + \lim_{r_1 \to R} |R - r_1| [\hat{v}_{co}^r(r_1, \omega)]_{ex} \psi_{r_\sigma}^{r}(r_1, \omega) = 0, \] (87)
where
\[ \tilde{C}^{x_\sigma}_{w_\sigma} = \delta_{w_\sigma,x_\sigma} + C^{x_\sigma}_{w_\sigma}. \] (88)

Since both terms from the above identity are independent, apparently, we must have
\[ \lim_{|r - R| \to 0} |R - r| \hat{h}_{v_1} \psi_{x_\sigma}^{r}(x) = 0, \] (89)
\[ \lim_{|r - R| \to 0} |R - r| \hat{h}_{v_1} \psi_{r_\sigma}^{r}(x) = 0. \] (90)

Substituting these relations into Eq. (84) proves that Eq. (83) is an identity. Hence, the density of the Brueckner-determinantal state, \(|\tau\rangle\), can be used to determine the external potential \( v \), Eq. (2), by using Eq. (29). Note that Eq. (89) is identical to Eq. (9), the cusp
condition, except that the orbitals are now Brueckner; Eq. (89) can also be used to prove all relations within Sec. II that appear after Eq. (9), including the one above that states that the density of the Brueckner-determinantal state can be used to determine the external potential.

VI. ONE-PARTICLE DENSITY-MATRIX THEORY

A. Variational Brueckner orbital theory

Reference-state one-particle density-matrix theory [30, 31, 34] is based on Brueckner orbital theory [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. Unlike many other density functional formalisms based on variants of the Kohn–Sham method, the correlation operator for this approach is non-local. The approach also uses an energy functional that depends on the one-particle density-matrix of a reference determinantal-state, and not the exact one from the target state, where the energy functional is partitioned into the exact exchange-energy and a correlation-energy functional that is non-universal, since this functional depends on the external potential $v$. We now modify this formalism to remove – for the most part – the dependence of the correlation energy-functional upon the external potential. However, an additional term that describes a portion of the potential energy is also included that does not have an analog in Kohn–Sham approaches. However, this term can be easily treated once the kinetic energy functional is known or, in many cases, this term can be neglected, since it is probably quite small. For convenience, we refer to the previous works [30, 31, 34] as being $v$-dependent, even though we still retain some $v$-dependence in the correlation-energy functionals for the current approach under consideration.

In this previous work [30, 31, 34], we introduced four $v$-dependent trial wavefunctions – say $|\Psi^{(\eta)}_{\gamma v}\rangle$, where $(\eta = I, II, III, and IV)$ – that are defined with respect to an external potential $v$ and a one-particle density-matrix, where $\gamma$ is from a single-determinantal reference-state, $|\gamma\rangle$.

The first trial-wavefunction $|\Psi^{(I)}_{\gamma v}\rangle$ is simply the target state of interest, say $|\Psi_{Nv}\rangle$, with the single excitations removed:

$$|\Psi^{(I)}_{\gamma v}\rangle = (1 - P_{11}^\gamma) |\Psi_{Nv}\rangle,$$

where $|\Psi_{Nv}\rangle$ is a ground-state determined by the external potential $v$ and the number of
electrons $N$ and, furthermore, the spin-conserved projector for the singly-excited states is

$$P_{11}^\gamma = \sum_{w\sigma \in \{\psi_o \rightarrow \gamma\}} \sum_{r\sigma \in \{\psi_u \rightarrow \gamma\}} |\gamma_{w\sigma}^r\rangle \langle \gamma_{w\sigma}^r|,$$  \hspace{1cm} (92)$$

where we assume that Eq. (67) holds, but this requirement can easily be dropped by appending the states $|\gamma_{w\sigma}^{r'}\rangle$ the the right side of Eq. (92). Note that the $P_{11}^\gamma$ subspace is completely determined by $|\gamma\rangle$; $P_{11}^\gamma$ is also invariant to a unitary transformation of occupied, or virtual, orbitals [13].

We now require the state $|\gamma\rangle$ to be a member of $\{|\gamma\rangle_v\}$, so Eq. (91) becomes

$$|\Psi^{(1)}_{\gamma v'}\rangle = (1 - P_{11}^\gamma) |\Psi_{N v'}\rangle, \quad \gamma \in \{|\gamma\rangle_v\}, \quad \gamma \rightarrow v, \quad \gamma \rightarrow N,$$  \hspace{1cm} (93)$$

where the prime superscripts appended to the external potentials, i.e., $v'$, emphasizes that the potential defining the states, $|\Psi^{(1)}_{\gamma v'}\rangle$ and $|\Psi_{N v'}\rangle$, may differ from the one determined by $\gamma$ (indicated by $\gamma \rightarrow v$). However, we now restrict these potentials to be equivalent, i.e., ($v' = v$), and generate the target state using a wave operator:

$$|\Psi^{(1)}_{\gamma v}\rangle = (1 - P_{11}^\gamma) |\Psi_{N v}\rangle = (1 - P_{11}^\gamma) \Omega_{\gamma v} |\gamma\rangle, \quad \gamma \in \{|\gamma\rangle_v\}, \quad \gamma \rightarrow v,$$  \hspace{1cm} (94)$$

and since the external potential is a unique function of $\gamma$ (or the density $\rho$ of $\gamma$), we can use the function $v(\gamma)$ to express the wave operator as a unique function of $\gamma$:

$$\Omega_{\gamma v} = \Omega_{\gamma}, \quad \gamma \in \{|\gamma\rangle_v\}, \quad \gamma \rightarrow v, \quad \gamma \rightarrow N,$$  \hspace{1cm} (95)$$

and for are target state, we have

$$|\Psi_{\gamma}\rangle = |\Psi_{N v}\rangle, \quad \gamma \rightarrow v, \quad \gamma \rightarrow N.$$  \hspace{1cm} (96)$$

Therefore, we are assuming that the target state is completely determined by $\gamma$. This is a reasonable assumption, since the Hamiltonian is completely determined by $\gamma$, since $\gamma$ gives the number of electrons, $N$, and the external potential $v$. In addition, however, we must also make the assumption that the wave operator is, or – at least, in principle – can be uniquely defined so that it generates only one exact eigenstate – the ground state – from all $\gamma$ that have ($\gamma \rightarrow v$). This implies, however, two wavefunctions can differ only by a constant, say $c$, if they are obtained from density-matrices that determine the same external potential:

$$|\Psi_{\gamma}\rangle = c |\Psi_{\gamma'}\rangle, \quad \text{if } \gamma \rightarrow v, \gamma' \rightarrow v', \text{ and } v = v'.$$  \hspace{1cm} (97)$$
where the $\gamma$ subscript also indicates the normalization of the target state:

$$\langle \gamma | \Psi_\gamma \rangle = 1.$$  \hfill (98)

By substituting Eqs. (95) and (96) into (94), we obtain a trial wavefunction that can be assumed to be determined by $\gamma$:

$$|\Psi_\gamma^{(I)}\rangle = (1 - P_{\gamma 11}) \Omega_\gamma |\gamma\rangle = (1 - P_{\gamma 11}^\gamma) |\Psi_\gamma\rangle, \quad \gamma \in \{ |\gamma\rangle_v \},$$  \hfill (99)

and we have

$$|\Psi_\gamma^{(I)}\rangle = c |\Psi_\gamma^{(I)}\rangle, \quad \text{if } \gamma \rightarrow v, \gamma' \rightarrow v', \text{ and } v = v',$$  \hfill (100)

$$\langle \gamma | \Psi_\gamma^{(I)} \rangle = 1.$$  \hfill (101)

The second trial-wavefunction $|\Psi_\gamma^{(II)}\rangle$ is defined with respect to the target state expressed by an exponential ansatz: $(|\Psi\rangle = e^{S_\gamma} |\gamma\rangle)$, where $|\Psi_\gamma^{(II)}\rangle$ is generated by removing the single-excitation amplitudes $S_\gamma^1$ from the cluster-operator $S$:

$$|\Psi_\gamma^{(II)}\rangle = e^{(S_\gamma - S_\gamma^1)} |\gamma\rangle,$$  \hfill (102)

where, as in Eq. (95), we have

$$S_{\gamma v} = S_\gamma \quad \gamma \in \{ |\gamma\rangle_v \}, \quad \gamma \rightarrow v, \quad \gamma \rightarrow N.$$  \hfill (103)

The third trial-wavefunction $|\Psi_\gamma^{(III)}\rangle$ can be generated by its wave-operator:

$$\hat{\Omega}_\gamma |\gamma\rangle = |\Psi_\gamma^{(III)}\rangle,$$  \hfill (104)

that can be expressed in an exponential form: $(\hat{\Omega}_\gamma = e^{\hat{S}_\gamma} |\gamma\rangle)$, where $\hat{S}_\gamma$ can be written as a sum $n$-body excitations, with the exclusion of a one-body operator:

$$\hat{S}_\gamma = \hat{S}_2^\gamma + \hat{S}_3^\gamma + \cdots.$$  \hfill (105)

The wave operator $\hat{\Omega}_\gamma$ is a solution to the coupled cluster equations \cite{27, 28, 29, 35, 36, 37, 38, 39, 40, 41} with the single excitation portion removed:

$$(1 - P_{\gamma 11}^\gamma) \left( H_v \hat{\Omega}_\gamma \right)_{op,cn} = 0, \quad \gamma \rightarrow v, \quad \gamma \rightarrow N,$$  \hfill (106)

where only the open (op) and connected (cn) portions enter into the relation. This expression defines the trial functional $|\Psi_\gamma^{(III)}\rangle$ using Eq. (104) and, again, Eq. (95) is satisfied with $\hat{\Omega}_\gamma$ replacing $\Omega_\gamma$. 

17
The fourth trial wavefunctions $|\Psi^{(IV)}_\gamma\rangle$ is not considered here, except to mention that it is obtained by solving the configuration-interaction equations [3, 41, 42] in an approximate way, i.e., by neglecting the single-excitation portion.

All of the trial states $|\Psi^{(\eta)}_\gamma\rangle$ share the property that they contain no single excitations, i.e., $(P_{11}^\gamma|\Psi^{(\eta)}_\gamma\rangle = 0)$, and they generate the target state $|\Psi_\tau\rangle$ when their reference state satisfies $(|\gamma\rangle = |\tau\rangle)$, where $|\tau\rangle$ is the determinantal state constructed from occupied Bruckner orbitals. In other words, we have

$$|\Psi^{(\eta)}_\tau\rangle = |\Psi_\tau\rangle.$$  \hfill (107)

Since the target state is a solution of the Schrödinger equation [55] with an exact energy, say $E_{Nv}$, we have

$$E_{Nv} = \langle \Psi_\gamma | H_v | \Psi_\gamma \rangle = E_1[\gamma, v] + E_{co}[\gamma, v] = \langle H_v \rangle_\gamma,$$  \hfill (108)

where the first-order energy $E_1$ is given by the expectation value of the Hamiltonian involving the reference state, $\langle \gamma| H_v | \gamma \rangle$, and the correlation energy $E_{co}$ is defined above as $(E_{Nv} - E_1)$; furthermore, the introduced notation $\langle H_v \rangle_\gamma$ indicates the expectation value of the Hamiltonian involving the target state $|\Psi_\gamma\rangle$.

Using the trial wavefunctions, we can define variational energy-functionals that depend on the one-particle density-matrix:

$$\tilde{E}_\eta[\gamma, v] = \langle H_v \rangle_{\eta \gamma} = E_1[\gamma, v] + \tilde{E}_{co}^{(\eta)}[\gamma, v],$$  \hfill (109)

where we use the notation for the expectation value of an operator, say $\hat{A}$, given by

$$\langle \hat{A} \rangle_{\eta \gamma} = \frac{\langle \Psi^{(\eta)}_\gamma | \hat{A} | \Psi^{(\eta)}_\gamma \rangle}{\langle \Psi^{(\eta)}_\gamma | \Psi^{(\eta)}_\gamma \rangle}$$  \hfill (110)

and the last relation within Eq. (109) defines the correlation-energy functionals $\tilde{E}_{co}^{(\eta)}$ as $(\tilde{E}_\eta - E_1)$; furthermore, the first order energy is given by

$$E_1[\gamma, v] = \int [-\frac{1}{2} \nabla_r^2 \rho_1(r, r')\big]_{r=r'} \; dr + \int v(r) \rho(r) \; dr + E_J[\rho] + E_x[\rho^\sigma_1],$$  \hfill (111)

where the Coulomb and exchange energies have their usual forms:

$$E_J[\rho] = \frac{1}{2} \int \int dr_1 dr_2 r_{12}^{-1} \rho_1(r_1) \rho_1(r_2),$$  \hfill (112)

$$-E_x[\rho^\sigma_1] = \frac{1}{2} \int \int dr_1 dr_2 r_{12}^{-1} \left( \rho^\sigma_1(r_1, r_2) \rho^\sigma_1(r_2, r_1) + \rho^\beta_1(r_1, r_2) \rho^\beta_1(r_2, r_1) \right),$$  \hfill (113)
and the spin-components of the one particle density matrix are given by

\[ \rho_\alpha^\beta(r_1, r_2) = \sum_{x \in \{\psi_\alpha \rightarrow \psi_\beta \}} \chi_{\alpha x}(r_1)(\chi_{\alpha x}(r_2))^* = \gamma(r_1, 1, r_2, 1), \]

(114)

\[ \rho_\beta^\alpha(r_1, r_2) = \sum_{x \in \{\psi_\beta \rightarrow \psi_\alpha \}} \chi_{\beta x}(r_1)(\chi_{\beta x}(r_2))^* = \gamma(r_1, -1, r_2, -1). \]

(115)

Substituting Eq. (111) into (109) gives the following:

\[
\bar{E}_\eta[\gamma, v] = \int \left[ -\frac{1}{2} \nabla^2_r \gamma(x, x') \right]_{x' = x} \, dx + \int v(r) \rho(r) \, dr + E_{J}[\rho] + \bar{E}_{xc}^{(n)}[\gamma, v],
\]

(116)

where the exchange-correlation energy-functionals are defined by

\[
\bar{E}_{xc}^{(n)}[\gamma, v] = E_{x}[\gamma] + \bar{E}_{co}^{(n)}[\gamma, v].
\]

(117)

Returning to our energy functionals, Eq. (109), let the functional derivative of these functionals yield two-body functions that serve as the kernels of exact Fock operators:

\[
\zeta_{\gamma v}^{(n)}(x_1, x_2) = \frac{\bar{E}_\eta[\gamma, v]}{\delta \gamma(x_2, x_1)} = \delta(x_2 - x_1) \left( -\frac{1}{2} \nabla^2_x + v(r_2) + \int r_{23}^{-1} \gamma(x_3, x_3) \, dx_3 \right) + \nu_{xc}^{(nv)}(x_1, x_2),
\]

(118)

where the kernels of the exchange-correlation operators, \( \nu_{xc}^{(nv)}(x_1, x_2) \), are obtained from the exchange-correlation energy-functionals:

\[
\nu_{xc}^{(nv)}(x_1, x_2) = \frac{\delta \bar{E}_{xc}^{(n)}[\gamma, v]}{\delta \gamma(x_2, x_1)} = \frac{\delta \bar{E}_{co}^{(n)}[\gamma, v]}{\delta \gamma(x_2, x_1)} - \tilde{n}_{12}^{-1} \gamma(x_1, x_2),
\]

(119)

where the last relation uses Eqs. (117) and the identity:

\[
\frac{\delta E_{x}[\gamma]}{\delta \gamma(x_2, x_1)} = -\tilde{n}_{12}^{-1} \gamma(x_1, x_2) = v_{x}^{(n)}(x_1, x_2),
\]

(120)

and the function \( v_{x}^{(n)}(x_1, x_2) \) is the kernel of the exchange operator, denoted by \( \hat{v}_{x}^{(n)} \).

Using the variation theorem, and by noting the identity given by Eq. (107), it becomes obvious – as in our previous \( v \)-dependent approach \([30, 31]\) – that the minimizing of the functionals \( \bar{E}_{\eta}[\gamma, v] \), subject to the constraint that the one-particle density-matrix comes from a single-determinantal state, yields

\[
\mathcal{E}_{Nv} = \bar{E}_{\eta}[\tau, v],
\]

(121)

\[
\mathcal{E}_{co}[\tau, v] = \bar{E}_{co}^{(n)}[\tau, v].
\]

(122)
where $\mathcal{E}_N$ and $\mathcal{E}_c$ are the electronic-energy and correlation energy arising from the target state, defined by Eqs. (105); furthermore, $\tau$ is the one-particle density-matrix of the Brueckner reference-state $|\tau\rangle$ that determines $\nu$:

$$\tau(x, x') = \sum_{w \in \{\psi_o \rightarrow \tau\}} \psi_w^*(x)\psi_w^r(x'), \ \tau \rightarrow \nu,$$

and the Brueckner orbitals satisfy the following equivalent conditions:

$$\langle \psi_r | \hat{\zeta}_\tau^{(\nu)} | \psi_w \rangle = 0; \ \psi_w \in \{\psi_o \rightarrow \tau\}, \ \psi_r \in \{\psi_u \rightarrow \tau\}, \ \tau \rightarrow \nu,$$

$$(\hat{1} - \tau) \hat{\zeta}_\tau^{(\nu)} \tau = 0,$$

where these orbitals do not depend on $\eta$—any trial wavefunction gives the same results.

A unique set of occupied and unoccupied orbitals is obtained by requiring the occupied and unoccupied blocks of $\hat{\zeta}_\tau^{(\nu)}$ to be diagonal:

$$\hat{\zeta}_\tau^{(\nu)} \psi_w^r(x) = \xi_\tau^r \psi_w^r(x), \ \psi_w^r \in \{\psi_o \rightarrow \tau\}, \ \tau \rightarrow \nu,$$

$$(\hat{1} - \tau) \hat{\zeta}_\tau^{(\nu)} \tau = 0,$$

Henceforth, the orbitals sets that satisfy Eqs. (124) and (125) are denoted by $\{\psi_o \leftarrow \hat{\tau}, \hat{\zeta}_\tau^{(\nu)}\}$ and $\{\psi_u \leftarrow \hat{\tau}, \hat{\zeta}_\tau^{(\nu)}\}$, indicating that they are determined by $\tau$ and $\hat{\zeta}_\tau^{(\nu)}$. Since these orbitals, and their energies, can, perhaps, depend on $\eta$, it is more precise to denote them by $\psi_{\nu}^{\tau\eta}$ and $\xi_{\tau\eta}^r$, but we suppress the $\eta$ superscripts to keep the notation less cluttered.

Substituting Eq. (118) into Eqs. (125) gives generalized, canonical Hartree–Fock Eqs:

$$\left(-\frac{1}{2} \nabla_1^2 + v(r_1) + \int r_{12}^{-1} \tau(x_2, x_2') d\mathbf{x}_2 + \hat{\nu}_{xc}^{\nu}(x_1)\right) \psi_\nu^r(x_1) = \xi_\nu^r \psi_\nu^r(x_1).$$

VII. TREATMENT OF THE CORRELATION-ENERGY FUNCTIONALS $\bar{\mathcal{E}}_{c0}^{(\nu)}$

The Hamiltonian operator $H_\nu$ can be written in normal-ordered form with respect to the reference state $|\gamma\rangle$:

$$H_\nu = E_1[\gamma, \nu] + \{v\}_{\gamma} + \left\{ -\frac{1}{2} \nabla^2 \right\}_{\gamma} + \left\{ r_{12}^{-1} \right\}_{\gamma},$$

(127)
where \{v\}_\gamma, \{-\frac{1}{2} \nabla^2\}_\gamma, and \{r^{-1}_{12}\}_\gamma are terms from the external potential, kinetic energy and electron-electron interactions:

\[
\{v\}_\gamma = \sum_{i\sigma j\sigma}(i\sigma|v|j\sigma)\{a^\dagger_{i\sigma}a_{j\sigma}\}_\gamma, \tag{128}
\]

\[
\{-\frac{1}{2} \nabla^2\}_\gamma = \sum_{i\sigma j\sigma}(i\sigma|-\frac{1}{2} \nabla^2|j\sigma)\{a^\dagger_{i\sigma}a_{j\sigma}\}_\gamma, \tag{129}
\]

\[
\{r^{-1}_{12}\}_\gamma = \frac{1}{2} \sum_{i\sigma j\sigma k\sigma' l\sigma'}(i\sigma j\sigma|k\sigma' l\sigma')\{a^\dagger_{i\sigma}a_{k\sigma}a_{l\sigma'}a_{j\sigma}\}_\gamma + \sum_{i\sigma j\sigma}(i\sigma|\hat{v}^\alpha + \hat{v}^\gamma)|j\sigma)\{a^\dagger_{i\sigma}a_{j\sigma}\}_\gamma, \tag{130}
\]

Furthermore, the Coulomb \(\hat{v}^\alpha\) operator satisfies:

\[
\hat{v}^\alpha\phi(r_1) = \int r^{-1}_{12} \rho(r_2) \phi(r_1) \, dr_2, \tag{131}
\]

and the exchange operator \(\hat{v}^\gamma\) is given by Eq. 43.

Substituting Eqs. (127) into (109) gives

\[
\bar{E}^{(o)}_{\text{co}}[\gamma, v] = V^{(o)}_{\text{co}}[\gamma, v] + T^{(o)}_{\text{co}}[\gamma] + U^{(o)}_{\text{co}}[\gamma] \tag{132}
\]

where these terms are identified as the potential, kinetic, and electron-electron-interaction contributions to the correlation-energy functionals:

\[
V^{(o)}_{\text{co}}[\gamma, v] = \langle \{v\}_\gamma \rangle_{\gamma \gamma} = \langle \{v\}_\gamma \rangle_{\gamma \gamma} \tag{133}
\]

\[
T^{(o)}_{\text{co}}[\gamma] = \langle \{-\frac{1}{2} \nabla^2\}_\gamma \rangle_{\gamma \gamma} = \langle \{-\frac{1}{2} \nabla^2\}_\gamma \rangle_{\gamma \gamma}, \tag{134}
\]

\[
U^{(o)}_{\text{co}}[\gamma] = \langle \{r^{-1}_{12}\}_\gamma \rangle_{\gamma \gamma} = \langle \{r^{-1}_{12}\}_\gamma \rangle_{\gamma \gamma}, \tag{135}
\]

and where we have also introduced a more condensed notation where the vacuum state is understood to agree with the trial wavefunction.

Similarly, substituting Eqs. (127) into (108) gives

\[
\mathcal{E}_{\text{co}}[\gamma, v] = V_{\text{co}}[\gamma, v] + T_{\text{co}}[\gamma] + U_{\text{co}}[\gamma] \tag{136}
\]

where

\[
V_{\text{co}}[\gamma, v] = \langle \{v\}_\gamma \rangle, \tag{137}
\]

\[
T_{\text{co}}[\gamma] = \langle \{-\frac{1}{2} \nabla^2\}_\gamma \rangle \tag{138}
\]

\[
U_{\text{co}}[\gamma] = \langle \{r^{-1}_{12}\}_\gamma \rangle. \tag{139}
\]
VIII. APPROXIMATIONS

If we know the exact correlation energy $E_{\text{co}}$ for some Brueckner one-particle density-matrix, say $\tau'$ with some external potential, say $v'$, where $\tau' \rightarrow v'$, then using Eq. (122), we obtain the following reasonable approximation:

$$\bar{E}_{\text{co}}^{(III)}[\gamma, v] = E_{\text{co}}[\tau', v']_{(\tau' = \gamma, v' = v)}, \quad \tau' \rightarrow v', \tag{140}$$

where a similar approximation has been used previously in the $v$-dependent approach [30, 31, 34], and we are assuming, as we have previously, that this approximation is most appropriate for $(\eta = \text{III})$. Similarly, a reasonable approximation for the components of the correlation-energy functionals are given by the following prescriptions:

$$V_{\text{co}}^{(III)}[\gamma, v] = V_{\text{co}}[\tau', v']_{(\tau' = \gamma, v' = v)}, \quad \tau' \rightarrow v', \tag{141}$$

$$T_{\text{co}}^{(III)}[\gamma] = T_{\text{co}}[\tau']_{(\tau' = \gamma)} \tag{142}$$

$$U_{\text{co}}^{(III)}[\gamma] = U_{\text{co}}[\tau']_{(\tau' = \gamma)}, \tag{143}$$

and the three functionals: $V_{\text{co}}, T_{\text{co}}$ and $U_{\text{co}}$, are known for a Brueckner one-particle density-matrix $\tau'$ that determines the external potential $v'$, i.e., $\tau' \rightarrow v'$. Of course, we have many Brueckner one-particle density-matrices $\tau$ coming from the same external potential $v$; presumable, we have one $\tau$ from each $N$-electron sector of the Hilbert space, for external potentials $v$ with nondegenerate ground states.

The correlation-energy functionals $E_{\text{co}}^{(\eta)}$ dependence on the external potential $v$ comes exclusively form the correlated potential-energy-functional $V_{\text{co}}^{(III)}$. In many cases it is reasonable to assume that the this functionals, and the kinetic energy one $T_{\text{co}}^{(III)}$, are small, since the potential- and kinetic-energy contributions are treated well in first order. Therefore, the following approximation seems reasonable:

$$\bar{E}_{\text{co}}^{(III)}[\gamma] \approx U_{\text{co}}[\tau']_{(\tau' = \gamma)}, \tag{144}$$

and this approximation yields a universal functional in the Kohn–Sham sense – the functional does not depend on $v$. However, even the potential energy contribution to the correlation-energy functional, $V_{\text{co}}^{(\eta)}$, can be viewed – in a more general sense – as being universal, since if this functional is known for an arbitrary external potential, than it is known for other cases, since the manner in which this functional depends on the external potential is the same for
all systems. On the other hand, if we use a model system to approximate the functionals, this will certainly not generate exact functionals for real systems, only approximation ones.

Using the helium atom as a model system where $U_{co}$ is presumable known, the previous approximation becomes

$$E_{co}^{(ii)}[\gamma] \approx U_{co}[^{[\tau_{ms}=\gamma]}],$$  \hspace{1cm} (145)$$

where $\tau_{ms}$ is the Brueckner one-particle density matrix from the helium atom. Assuming the Hartree–Fock one-particle density-matrix, say $\tilde{\tau}_{ms}$, is approximately equal to the Brueckner one, $\tau_{ms}$, we have

$$E_{co}^{(ii)}[\gamma] \approx U_{co}[\tilde{\tau}_{ms}](\tilde{\tau}_{ms}=\gamma),$$  \hspace{1cm} (146)$$

and for a closed-shell systems that use spatially-restricted spin-orbitals, given by Eq. (145), we have

$$E_{co}^{(ii)}[\rho_1] \approx U_{co}[\tilde{\rho}_{ms}](\tilde{\rho}_{ms}=\rho_1),$$  \hspace{1cm} (147)$$

where $\rho_1$ is the spinless one-particle density matrix [2, 43], given by Eq. (A1). As demonstrated in Appendix A, we can use the well known approximation for $U_{co}^{cs}[\tilde{\rho}_{ms}]$ given by the Colle and Salvetti functional [44, 45], giving

$$E_{co}^{(ii)}[\rho_1] \approx E_{co}^{cs}[\rho_1] = U_{co}^{cs}[\tilde{\rho}_{ms}](\tilde{\rho}_{ms}=\rho_1),$$  \hspace{1cm} (148)$$

where this functional, denoted by $E_{co}^{cs}$, uses four empirical parameters that are determined using data from the helium atom. In addition, it is readily verified that this approximate correlation-energy functional neglects the potential- and kinetic-energy components, $V_{co}$ and $T_{co}$, and these terms vanish when the exact one-particle density matrix, say $\Gamma_1$, from the target state $|\Psi_\gamma\rangle$, is equal to the reference state one, $\gamma$; these two terms are considered to be small, or small enough to neglect, when $(\Gamma_1 \approx \gamma_1)$, as in the approach used when deriving the Colle–Salvetti functional. (Note that $V_{co}$ vanishes if the density from the reference-state is the same as the density from the target state, as is the case for the Kohn–Sham method.)

Using an identical derivation as in the $v$-dependent approach [34], it is readily verified that the well known density-dependent approximation for the Colle–Salvetti functional [45], given by the LYP functional – at least for closed shell ground states – remains valid for the current approach:

$$E_{co}^{cs}[\rho] \approx E_{co}^{LYP}[\rho],$$  \hspace{1cm} (149)$$
where the density $\rho$ dependence is associated with the reference state, and not the target state.

An electron gas defined by an constant external potential is not a member of $\{ |\gamma\rangle_v \}$, as in the case for an electron gas with periodic boundary conditions. However, let us assume that we can generalize the functional $v(\rho)$ so that it yields the appropriate constant value, say $v_g$, from the constant-density of an electron gas, say $\rho_g$; so, we have $v(\rho_g) = v_g$. And if we denote the one-particle density-matrix of the Brueckner reference state for an electron gas by $\tau_g$, we get

$$\bar{E}^{(III)}_{co}[\gamma, v] \approx E_{co}[\tau_g, v_g] (\tau_g = \gamma, v_g = v).$$

(150)

However, since the correlation energy $E_{co}$ does not depend on on the constant external potential $v_g$, we cannot make the substitution ($v_g = v$), and so we obtain an approximation that yields a universal functional:

$$\bar{E}^{(III)}_{co}[\gamma] \approx E^{(gas)}_{co}[\tau_g] (\tau_g = \gamma),$$

(151)

where $E^{(gas)}_{co}$ is the correlation energy of an electron gas, and this approximation is also identical to the approximation used in the $v$-dependent approach [30, 31], but with a slightly different interpretation and derivation. Furthermore, in order to include $\tau_g$ in the set $\{ |\gamma\rangle_v \}$, we only need to require $v(\rho)$ to vanishes for any constant density: $v(\rho_g) = 0$, where we consider two external-potentials that differ by a constant to be equivalent.

Starting with Eq. (151), except using a uniform electron gas, the same correlation energy-function used in the local density approximation (LDA) [46] was shown to be valid with the $v$-dependent approach, for closed shell ground states [34]; however, in contrast to the Kohn–Sham approach, the density dependence of the correlation-energy function is only associated with the reference state, and not, in addition, the target state. Furthermore, using an identical derivation as in the $v$-dependent approach, it is easily verified that the correlation-energy functional from LDA can also be used, as well, as an approximation for $\bar{E}^{(III)}_{co}$ within the current approach under consideration. Furthermore, since the exchange-energy functional in the current approach is identical with the one from the $v$-dependent method, the exchange-energy functionals that are valid in the $v$-dependent approach are also valid in the current approach, including the Dirac exchange-functional, and the augmentation of this functional with the Becke exchange correction [47]. Hence, as in the $v$-dependent approach, the LDA
and the method known as BLYP are also valid in the current method. (At least for closed shell ground states.) Furthermore, it is readily verified that the B3LYP approach \[48, 49\] — that was demonstrated to be a reasonable approximation within the \(v\)-dependent approach for closed-shell ground-states \[34\] — remains valid for current approach under consideration.

While all functionals that have been shown, so far, to be valid approximations for the \(v\)-dependent approach, are also valid in the current approach, the use of the LYP and Colle–Salvetti functional appear more natural within the current approach under consideration, since these functionals are universal ones that do not have a dependence on the external potential. And since the BLYP and B3LYP functionals contain the LYP functional, these approaches are also better suited with the current approach.

**APPENDIX A: CONNECTION WITH COLLE–SALVETTI FUNCTIONAL**

In order to keep the discussion simple, we only consider closed-shell singlet states that are well described by a single determinantal-state, where we use spatially-restricted spin-orbitals, given by

\[
\psi_{j\sigma}(\mathbf{x}) = \chi_j(\mathbf{r}) \sigma(\omega); \quad \sigma = \alpha, \beta.
\]  

(A1)

By using these orbitals, it is easily demonstrated that the one-particle density-matrix \(\gamma\) is determined by the spinless one, as indicated by the following relation:

\[
\gamma(x_1, x_2) = \frac{1}{2} \rho_1(r_1, r_2) \delta_{\omega_1, \omega_2}.
\]  

(A2)

Hence, any functional of \(\gamma\) now becomes a functional of \(\rho_1\); So, if we use the Hartree–Fock spin-less one-particle density matrix, say \(\tilde{\rho}_1\), Eq. (108), becomes

\[
\mathcal{E}_{Nv} = E_1[\tilde{\rho}_1, v] + \mathcal{E}_{co}[\tilde{\rho}_1, v].
\]  

(A3)

Substituting Eq. (136) into this expression for \((\gamma_1 = \rho_1)\), and neglected the terms \(V_{co}\) and \(T_{co}\), we have

\[
\mathcal{E}_{Nv} \approx E_1[\tilde{\rho}_1, v] + U_{co}[\tilde{\rho}_1],
\]  

(A4)

and using Eq. (111), we have

\[
\mathcal{E}_{Nv} \approx \int \left[ -\frac{1}{2} \nabla^2 \tilde{\rho}_1(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r} = r} d\mathbf{r} + \int v(\mathbf{r}) \tilde{\rho}(\mathbf{r}) d\mathbf{r} + E_1[\tilde{\rho}] + E_x[\tilde{\rho}^2] + U_{co}[\tilde{\rho}_1].
\]  

(A5)
Consider the total electron-electron potential energy, given as the expectation value involving the target state $|\Psi_{\rho_1}\rangle$ and the electron-electron repulsion energy operator $\{r^{-1}_{12}\}_0$:

$$\langle\{r^{-1}_{12}\}_0\rangle_{\gamma} = \frac{\langle\Psi_{\rho_1}|\{r^{-1}_{12}\}_0|\Psi_{\rho_1}\rangle}{\langle\Psi_{\rho_1}|\Psi_{\rho_1}\rangle}$$  \hspace{1cm} (A6)

where the operator is given by

$$\{r^{-1}_{12}\}_0 = \frac{1}{2} \sum_{i\sigma j\sigma' k\sigma' l\sigma'} (i\sigma j\sigma|k\sigma' l\sigma')a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma},$$  \hspace{1cm} (A7)

and the 0 subscript appended to $\{r^{-1}_{12}\}_0$ indicates normal-ordering with respect to the true vacuum state, $|\rangle$. Using the Hartree–Fock closed-shell reference-state $|\tilde{\rho}_1\rangle$, instead, as the vacuum-state, it is readily demonstrated that we have

$$\langle\{r^{-1}_{12}\}_0\rangle_{\tilde{\rho}_1} = \langle\{r^{-1}_{12}\}_{1,2}\rangle_{\tilde{\rho}_1} + E_I[\tilde{\rho}] + E_x[\tilde{\rho}_1] = U_{co}[\tilde{\rho}_1] + E_I[\tilde{\rho}] + E_x[\tilde{\rho}_1],$$  \hspace{1cm} (A8)

where we have used Eq. (139); in addition, $\{r^{-1}_{12}\}_{1,2}$ is given by Eq. (130), where the suppressed superscript, $\gamma$ – the vacuum state – is set to $\tilde{\rho}_1$.

It is well known that the total electron-electron potential energy can also be expressed using the (diagonal portion of) the two-particle, spinless density-matrix from the target state [2, 43]:

$$\langle\{r^{-1}_{12}\}_0\rangle_{\tilde{\rho}_1} = \int \int r^{-1}_{12} \Gamma_{2}^{\tilde{\rho}_1}(r_1, r_2) \, dr_1 dr_2,$$  \hspace{1cm} (A9)

and we can use the approximate expression, involving a two-body function $\varphi$, for the two-particle spinless-density-matrix – valid for closed-shell systems – that was derived by Colle and Salvetti [44]:

$$\Gamma_{2}^{\tilde{\rho}_1}(r_1, r_2) = \tilde{\rho}_2(r_1, r_2) \left(1 + \varphi^2(r_1, r_2) - 2\varphi(r_1, r_2)\right),$$  \hspace{1cm} (A10)

and the two-particle density-matrix, from the Hartree–Fock reference-state, is given by

$$\tilde{\rho}_2(r_1, r_2) = \frac{1}{2}\tilde{\rho}(r_1)\tilde{\rho}(r_2) - \frac{1}{4}\tilde{\rho}_1(r_1, r_2)\tilde{\rho}_1(r_2, r_1),$$  \hspace{1cm} (A11)

where we also have

$$\int \int r^{-1}_{12} \tilde{\rho}_2(r_1, r_2) \, dr_1 dr_2 = E_I[\tilde{\rho}] + E_x[\tilde{\rho}_1].$$  \hspace{1cm} (A12)

Substituting Eq. (A10) into (A9) and using (A12), we have

$$\langle\{r^{-1}_{12}\}_0\rangle_{\tilde{\rho}_1} = E_I[\tilde{\rho}] + E_x[\tilde{\rho}_1] + E^{cs}_{co}[\tilde{\rho}_1],$$  \hspace{1cm} (A13)
where $E_{cs}^{\text{co}}$ is the Colle–Salvetti correlation-energy functional \cite{44, 45}:

$$E_{cs}^{\text{co}}[\tilde{\rho}_1] = \int \int r_{12}^{-1} \tilde{g}_2(\mathbf{r}_1, \mathbf{r}_2) \left( \varphi^2(\mathbf{r}_1, \mathbf{r}_2) - 2 \varphi(\mathbf{r}_1, \mathbf{r}_2) \right),$$  \hspace{1cm} (A14)

and this functional, after a series of approximations, is developed into one that does depend explicitly on $\tilde{\rho}_1$ \cite{45}. (Note that $\tilde{\rho}_2$ is determined by $\tilde{\rho}_1$, as indicated by Eq. (A11).)

Comparing this Eqs. (A8) and (A13), gives the desired result:

$$E_{cs}^{\text{co}}[\tilde{\rho}_1] = U_{co}[\tilde{\rho}_1].$$  \hspace{1cm} (A15)

and from Eq. (A4), we have

$$\mathcal{E}_{Nv} = E_1[\tilde{\rho}_1, v] + E_{cs}^{\text{co}}[\tilde{\rho}_1],$$  \hspace{1cm} (A16)

in agreement with the Colle–Salvetti electronic energy expression used in their derivation of $E_{cs}^{\text{co}}$ \cite{44}, where $E_1[\tilde{\rho}_1, v]$ is the Hartree–Fock energy.

**APPENDIX B: DERIVATION OF Eq. (84)**

Using the occupied and unoccupied Brueckner orbitals, given by Eqs. (62) and (63), respectively, we can express the one-body operator $(\hat{v}_{co}^\tau)^\text{ex}$ in the following manner:

$$(\hat{v}_{co}^\tau)^\text{ex} = \sum_{w\sigma} \sum_{r\sigma} \langle r\sigma | (\hat{v}_{co}^\tau)^\text{ex} | w\sigma \rangle a_{r\sigma}^\dagger a_{w\sigma},$$  \hspace{1cm} (B1)

where, as in $(H_{\chi})_1$, the vanishing terms involving the matrix elements that do not preserve the spin state, i.e., $\langle r\sigma | (\hat{v}_{co}^\tau)^\text{ex} | w\sigma \rangle$ for $\sigma \neq \sigma'$, are omitted. The matrix elements in the above expression can be computed using the kernel from the operator:

$$\langle r\sigma | (\hat{v}_{co}^\tau)^\text{ex} | w\sigma \rangle = \int \int \psi_{R\tau\sigma}^r(\mathbf{x}) \nu_{co}^{\text{exc}}(\mathbf{x}, \mathbf{x}') \psi_{w\sigma}^r(\mathbf{x}') d\mathbf{x} d\mathbf{x}';$$  \hspace{1cm} (B2)

so, if we have the an expression for the matrix element on the left-hand side, that has the general form given by the integral on the right-hand side, we should by able to obtain the kernel $\nu_{co}^{\text{exc}}(\mathbf{x}, \mathbf{x}')$ and, therefore, $(\hat{v}_{co}^\tau)^\text{ex} \psi_{w\sigma}^r$, from the following definition:

$$(\hat{v}_{co}^\tau(\mathbf{x}))_{\text{ex}} \psi_{w\sigma}(\mathbf{x}) = \int \nu_{co}^{\text{exc}}(\mathbf{x}, \mathbf{x}') \psi_{w\sigma}(\mathbf{x}') d\mathbf{x}'.$$  \hspace{1cm} (B3)

In order to obtain an expression for the term on the left side of Eq. (86), below we obtain the diagrammatic expansion of the open portion of $(H_{\chi})_1$, where this operator gives the
matrix elements $\langle r\sigma^\prime | \hat{v}_{co} | w\sigma \rangle$ using Eqs. (79) and (B2). We then use this matrix element to determine $\hat{v}_{co} \psi_{w\sigma}^\tau$ and obtain the identity given by Eq. (84).

It is well known that the correlation operator $\chi^\tau$ is given by a linked-diagram expansion, where all disconnected pieces are open [29, 38, 50]. Since $\chi^\tau$ does not contain a one-body portion, it is easily demonstrated that the open portion of $(H\chi^\tau)_1$ is connected – all disconnected pieces from $\chi^\tau$ are connected by the Hamiltonian $H$.

Using the diagrammatic formalism presented in Appendix C and elsewhere [30], consider the following example of a diagram that contributes to the open portion of $(H\chi^\tau)_1$:

$$\hat{F}_{r\tau_1} \kappa^\tau (x_1, x_2) g(x_2, x_1^\prime) \psi_{w\sigma}^\tau (x_1^\prime) \psi_{r\sigma}^\tau (x_1) a^\dagger_{r\sigma} a_{w\sigma},$$  \hspace{1cm} (B4)

where the repeated indices, $w\sigma$ and $r\sigma$, are summed over and where the two body function is given by

$$g(x_2, x_1^\prime) = \frac{1}{16} \tilde{r}_1^{-4} \tau (x_4, x_5) \hat{F}_{r\tau_3} \kappa^\tau (x_5, x_6) \kappa^\tau (x_6, x_4) r_{62}^{-1} r_{41}^{-1} \kappa^\tau (x_2, x_3) \hat{F}_{r\tau_3} \kappa^\tau (x_3, x_1^\prime);$$  \hspace{1cm} (B5)

furthermore, it is understood that there are no integrations over $x_2$ and $x_1^\prime$ on the right side of Eq. (B5), since these variables are not repeated indices according to the following convention: When determining which dummy indices are repeated indices, indices appearing within operators are not counted. So, for example, the indices $x_2$ and $x_1^\prime$ appear only once in the above Eq, and not two times, since the dummy indices from the Coulombic operator, i.e., $x_2$ (and $x_6$) from $r_{62}^{-1}$ and $x_1^\prime$ (and $x_4$) from $r_{41}^{-1}$, are not counted.

The orbitals $\psi_{w\sigma}^\tau$ and $\psi_{r\sigma}^\tau$, presented in Eq. (B4), can be any Brueckner orbitals, as defined by Eqs. (62) and (63). However, for convenience we choose the canonical orbitals that are eigenfunctions of $\hat{F}_{r\tau}$, as defined by Eq. (82). Using these orbitals the Brueckner one-particle density-matrix, $\tau$, and the orthogonal function, $\kappa$, are given by

$$\tau(x, x') = \sum_{x\sigma \in \{ \psi_{w\sigma}^\tau \}} \psi_{x\sigma}^\tau (x) (\psi_{x\sigma}^\tau (x'))^*, \hspace{1cm} (B6)$$

$$\kappa(x, x') = \sum_{x\sigma \in \{ \psi_{r\sigma}^\tau \}} \psi_{x\sigma}^\tau (x) (\psi_{x\sigma}^\tau (x'))^*, \hspace{1cm} (B7)$$

where these functions are also given by Eqs. (64) and (65).
According to Eq. (79), the diagram from Eq. (B4) also contributes to \( (\hat{v}_{\text{co}}^e)_{\text{ex}} \). Comparing Eqs. (B1) and (B4) we see that the following term:

\[
\hat{F}_{\tau_1 \kappa_\tau}(x_1, x_2) g(x_2, x_{1'}^\tau) \psi_{w^\tau}^*(x_{1'}) \psi_{r^\tau}^*(x_1),
\]

contributes to the matrix element \( \langle r \mid (\hat{v}_{\text{co}}^e)_{\text{ex}} \mid w \rangle \); furthermore, and diagrammatically speaking, removing the incoming and outgoing free-lines from the operator given by Eq. (B4), yields

\[
\begin{align*}
\begin{array}{c}
\vdots \\
1 1' \\
\vdots
\end{array}
\end{align*} = \hat{F}_{\tau_1 \kappa_\tau}(x_1, x_2) g(x_2, x_{1'}),
\]

and this diagram contributes to \( v_{\text{co}}^{eex}(x_1, x_{1'}) \), the kernel of \( (\hat{v}_{\text{co}}^e)_{\text{ex}} \), as defined by Eq. (B2); furthermore, we use the following diagrammatic representation for this two-body function:

\[
v_{\text{co}}^{eex}(x_1, x_{1'}) = \begin{array}{c}
v_{\text{co}}^e
\end{array}
\]

where, in addition, the non-dummy indices \( x_1 \) and \( x_{1'} \) in the above two diagrams, by our convention, correspond to the vertices of the omitted outgoing and incoming lines, respectively. Note that we have labeled these indices in the diagrams above; however, we will often omit these labels in similar (kernel) diagrams below.

As a slight variation of the diagram given within Eq. (B4), consider the following diagram:

\[
\begin{align*}
\begin{array}{c}
\vdots \\
1 1' \\
\vdots
\end{array} = \frac{1}{2} \hat{F}_{\tau_1 \kappa_\tau}(x_1, x_2) g(x_2, x_{1'}) \psi_{w^\tau}^*(x_{1'}) \psi_{r^\tau}^*(x_1) a^d_1 a_w,
\end{align*}
\]

where the additional factor of \( \frac{1}{2} \) comes from the diagonal term, given by Eq. (C20a). As in the diagram within Eq. (B4), this diagram contributes to \( (\hat{v}_{\text{co}}^e)_{\text{ex}} \); the corresponding diagram that contributes to the kernel \( v_{\text{co}}^{eex}(x_1, x_{1'}) \) can be expressed in two alternative forms:

\[
\begin{align*}
\begin{array}{c}
\vdots \\
1 1' \\
\vdots
\end{array} = \begin{array}{c}
\vdots
\end{array} = \frac{1}{2} \hat{F}_{\tau_1 \kappa_\tau}(x_1, x_2) g(x_2, x_{1'}),
\end{align*}
\]

where the first diagram on the left side replaces the incoming and outgoing omitted-lines with dotted lines; this form gives a visual aid in determining the excitations involved and a pseudo hole-line for the diagonal term to reside on.
The diagrams appearing in Eqs. (B8) and (B11) are examples of one-body kernel-diagrams where the omitted outgoing free-line is attached at a $\hat{F}_{r_1}$ vertex and the omitted incoming-line is attached at the $x_{1'}$ vertex of a $r^{-1}_{ji'}$ operator. (In this particular case we have $(j = 4)$, according to Eq. (B5)). Furthermore, note that the Fock operator is acting upon excited orbitals, giving the $\hat{F}_{r_1}\kappa_{r}(x_1, x_2)$ term. Summing over all diagrams of this type, we have

$$\hat{F}_{r_1}\kappa_{r}(x_1, x_2)G(x_2, x_{1'})$$

(B12)

where the two-body function $G(x_2, x_{1'})$ is obtained from the infinite-order expansion, and, for brevity, we have only displayed the first four diagrams of the series. Introducing a diagrammatic symbol for $G(x_2, x_{1'})$, we can represent the above expansion in the following manner:

$$\hat{F}_{r_1}\kappa_{r}(x_1, x_2)G(x_2, x_{1'}) =$$

(B13)

As a slight variation of the diagrams from the series appearing in Eq. (B12), we also have diagrams that have the Fock operator acting upon occupied orbitals, e.g.,

$$\hat{F}_{r_1}\tau(x_1, x_2)g(x_2, x_{1'})$$

(B14)

where $g(x_2, x_{1'})$ is given by Eq. (B5). Summing over all diagrams of this type, as in Eqs. (B12) and (B13), we have

$$\hat{F}_{r_1}\tau(x_1, x_2)I(x_2, x_{1'}) =$$

(B15)

The diagram sums represented by Eqs. (B13) and (B15) include all diagram where the omitted outgoing free-line is attached at a $\hat{F}_{r_1}$ vertex and the omitted incoming-line is attached at the $x_{1'}$ vertex of a $r^{-1}_{ji'}$ operator. Two examples where both incoming and outgoing omitted-lines are connected to Fock operators are given by the following two diagrams:

$$\hat{F}_{r_1}\kappa_{r}(x_1, x_2)l(x_2, x_{1'})\hat{F}_{r_{1'}}$$

(B16)
\[ F_{\tau_1}(x_1, x_2) m(x_2, x_{1'}) \hat{F}_{\tau'_{1'}}, \]  

where, in these examples, we have

\[ l(x_2, x_{1'}) = \frac{1}{96} \varepsilon^{-4}_\tau (x_4, x_5) \hat{F}_{\tau_5} \kappa_\tau(x_5, x_6) \kappa_\tau(x_6, x_4) r^{-1}_{42} r^{-1}_{63} \tau(x_2, x_3) \kappa_\tau(x_3, x_{1'}), \]  

\[ m(x_2, x_{1'}) = \frac{1}{96} \varepsilon^{-4}_\tau (x_4, x_5) \hat{F}_{\tau_5} \kappa_\tau(x_5, x_6) \kappa_\tau(x_6, x_4) r^{-1}_{42} r^{-1}_{63} \kappa_\tau(x_2, x_3) \tau(x_3, x_{1'}), \]

and again, we can sum over all diagrams of these types:

\[ \hat{F}_{\tau_1} \kappa_\tau(x_1, x_2) L(x_2, x_{1'}) \hat{F}_{\tau'_{1'}} = \]  

\[ \hat{F}_{\tau_1} \tau(x_1, x_2) M(x_2, x_{1'}) \hat{F}_{\tau'_{1'}} = \]

The other two cases of interest involve diagrams where both incoming and outgoing omitted lines are attached to the two-body part of the Hamiltonian, e.g., \( r^{-1}_{ij} \), and diagrams where the omitted incoming free-line is attached at a \( \hat{F}_{\tau_{1'}} \) vertex and the omitted outgoing-line is attached at the \( x_1 \) vertex of a \( r^{-1}_{j1} \) operator. Examples of these two cases are given by the following two diagrams:

\[ p(x_1, x_{1'}) = \]  

\[ n(x_1, x_{1'}) \hat{F}_{\tau_{1'}} = \]

where, for these examples, we have

\[ p(x_1, x_{1'}) = \frac{1}{128} \varepsilon^{-4}_\tau (x_4, x_5) \hat{F}_{\tau_5} \kappa_\tau(x_5, x_6) \kappa_\tau(x_6, x_4) r^{-1}_{61'} r^{-1}_{41} \tau(x_1, x_2) \hat{F}_{\tau_2} \tau(x_2, x_3) \hat{F}_{\tau_3} \tau(x_3, x_{1'}). \]

\[ n(x_1, x_{1'}) = \frac{1}{16} \varepsilon^{-4}_\tau (x_4, x_5) \hat{F}_{\tau_5} \kappa_\tau(x_5, x_6) \kappa_\tau(x_6, x_4) r^{-1}_{63} r^{-1}_{41} \tau(x_1, x_2) \hat{F}_{\tau_2} \tau(x_2, x_3) \tau(x_3, x_{1'}). \]

Summing over all diagrams of these types, gives

\[ P(x_1, x_{1'}) = \]  

\[ N(x_1, x_{1'}) \hat{F}_{\tau_{1'}} = \]

31
Since the diagrams represented in Eq. (B13), (B15), (B20), (B21), (B26), and (B27) include all possible diagrams that can contribute to $v_{co}^{ex}(x_1, x_{1'})$, using these expression and Eq. (B30), we have the following diagrammatic and algebraic relations:

$$v_{co}^{ex}(x_1, x_{1'}) = \hat{F}_{r_1} \kappa_{r_1}(x_1, x_2) G(x_2, x_{1'}) + \hat{F}_{r_1} \tau(x_1, x_2) I(x_2, x_{1'}) + \hat{F}_{r_1} \kappa_{r_1}(x_1, x_2) L(x_2, x_{1'}) \hat{F}_{r_1}$$

$$+ \hat{F}_{r_1} \tau(x_1, x_2) M(x_2, x_{1'}) \hat{F}_{r_1} + P(x_1, x_{1'}) + N(x_1, x_{1'}) \hat{F}_{r_1}.$$  

Substituting this expression into Eq. (B3), and reordering terms, we have

$$v_{co}^{ex}(x_1, x_{1'}) = P(x_1, x_{1'}) \psi_{u\sigma}^r(x_{1'}) + N(x_1, x_{1'}) \hat{F}_{r_1} \psi_{u\sigma}^r(x_{1'})$$

Using a similar analysis, we also obtain the following identity:

$$\text{lim}_{r_1 \to R} |r_1 - R| P(x_1, x_{1'}) \psi_{u\sigma}^r(x_{1'}) = 0, \quad \text{for all } R,$$

where the variable $x_1$ within $P(x_1, x_2)$ is the independent variable for functions of the general form $r_{j1}^{-1} \tau(x_1, x_i)$ or $r_{j1}^{-1} \kappa_{r_1}(x_1, x_i)$, and the dummy indices in these function: $x_i$ and $x_j$, are integrated over; furthermore, and in general, all other variable that appear in diagrams that contribute to $P(x_1, x_{1'})$ – e.g., $x_1$, $x_2$, $x_3$, $x_4$, and $x_6$ for $p(x_1, x_{1'})$ as presented in Eq. (B34) – are also dummy integration variables. Hence, since the functions $r_{j1}^{-1} \tau(x_1, x_i)$ and $r_{j1}^{-1} \kappa_{r_1}(x_1, x_i)$ do not contain a laplacian term – i.e., $-\frac{1}{2} \nabla^2 r_1 \tau(x_1, x_i)$ or $-\frac{1}{2} \nabla^2 r_1 \kappa_{r_1}(x_1, x_i)$ – or a singularity – i.e., $|r_1 - R_m|^{-1}$ – the above identity holds.

Using a similar analysis, we also obtain the following identity:

$$\text{lim}_{r_1 \to R} |r_1 - R| N(x_1, x_{1'}) \hat{F}_{r_1} \psi_{u\sigma}^r(x_{1'}) = 0.$$  

Substituting Eq. (B30) into (S3), and using the above two identities, we get

$$\text{lim}_{r_1 \to R} |r_1 - R| [\hat{v}_{co}^{ex}(x_1)]_{ex} \psi_{u\sigma}^r(x_1) =$$

$$\text{lim}_{r_1 \to R} |r_1 - R| [\hat{F}_{r_1} \kappa_{r_1}(x_1, x_2) G(x_2, x_{1'}) \psi_{u\sigma}^r(x_{1'}) + \hat{F}_{r_1} \tau(x_1, x_2) I(x_2, x_{1'}) \psi_{u\sigma}^r(x_{1'})$$

$$+ \hat{F}_{r_1} \kappa_{r_1}(x_1, x_2) L(x_2, x_{1'}) \hat{F}_{r_1} \psi_{u\sigma}^r(x_{1'}) + \hat{F}_{r_1} \tau(x_1, x_2) M(x_2, x_{1'}) \hat{F}_{r_1} \psi_{u\sigma}^r(x_{1'})].$$

32
and this expression can be written as

$$
\lim_{r_1 \to R} |r_1 - R| [\hat{\psi}_{\text{co}}^r(x_1)]_{\text{ex}} \hat{\psi}_{w\sigma}^r(x_1) =
$$

$$
\lim_{r_1 \to R} |r_1 - R| \left[ \hat{F}_{r_1 \tau}(x_1, x_2) A_{w\sigma}(x_2) + \hat{F}_{r_1 \kappa\tau}(x_1, x_2) B_{w\sigma}(x_2) \right],
$$

where

$$
A_{w\sigma}(x_2) = I(x_2, x_{1'}) \psi_{w\sigma}^r(x_{1'}) + M(x_2, x_{1'}) \hat{F}_{r_{1'}} \psi_{w\sigma}^r(x_{1'}),
$$

$$
B_{w\sigma}(x_2) = G(x_2, x_{1'}) \psi_{w\sigma}^r(x_{1'}) + L(x_2, x_{1'}) \hat{F}_{r_{1'}} \psi_{w\sigma}^r(x_{1'}).
$$

Substituting into Eq. (B34) the Fock operator, Eq. (41), it is easily seen that the terms involving the Coulomb and exchange operator vanish, so we have

$$
\lim_{r_1 \to R} |r_1 - R| [\hat{\psi}_{\text{co}}^r(x_1)]_{\text{ex}} \hat{\psi}_{w\sigma}^r(x_1) =
$$

$$
\lim_{r_1 \to R} |r_1 - R| \left[ \hat{h}_{u1 \tau}(x_1, x_2) A_{w\sigma}(x_2) + \hat{h}_{u1 \kappa\tau}(x_1, x_2) B_{w\sigma}(x_2) \right],
$$

where \( \hat{h}_{u1} \) is given by Eq. (B35). Using Eqs. (63) and (65), we obtain Eq. (84), where

$$
C^{x\sigma}_{w\sigma} = A_{w\sigma}(x_2) (\psi_{x\sigma}^r(x_2))^* \quad \text{(B38)}
$$

$$
D^{r\sigma}_{w\sigma} = B_{w\sigma}(x_2) (\psi_{r\sigma}^r(x_2))^* \quad \text{(B39)}
$$

and the terms that do not preserve the spin state, e.g., \( D^{x\sigma'}_{w\sigma} \), are omitted, since these terms vanish; furthermore, there are summations over the repeated indices \( x\sigma \) and \( r\sigma \) for the orbital sets \( \{ \psi_o \leftarrow \tau, \hat{F}_\tau \} \) and \( \{ \psi_u \leftarrow \tau, \hat{F}_\tau \} \), respectively.

**APPENDIX C: DIAGRAMMATIC FORMALISM FOR THE CORRELATION ENERGY \( E_{\text{co}} \)**

In order to keep the notation less cluttered, for this section we use a combined spin-spatial notation for spin-orbital indices; for example, \( \psi_{w\sigma}^r \) is now denoted by \( \psi_{w\sigma}^r \).

A diagrammatic expansion for correlation-energy \( E_{\text{co}} \), or for \( \chi_\tau \) using Lindgren’s formalism \([29, 38, 50]\), is easier to obtain when all operators involved are written in normal-ordered form \([24, 28, 29, 51]\). For example, the Hamiltonian, given by Eq. (50), can be written as

$$
H = E_1[\tau] + \{ \hat{F}_\tau \} + \{ r_{12}^{-1} \}_\tau,
$$

\((C1)\)
where

\[ E_1[\tau] = \langle \tau | H | \tau \rangle = \sum_w [w|\hat{\tau}|w] + \frac{1}{2} \sum_{wx} ([ww|xx] - [wx|wx]), \quad \quad \text{(C2)} \]

\[ \{ \hat{F}_\tau \} = \sum_{ij} \left[ \hat{a}_i^\dagger \hat{a}_j \right] \{ \hat{a}_i^\dagger \hat{a}_j \}_\tau, \quad \text{(C3)} \]

\[ \{ r_{12}^{-1} \}_\tau = \frac{1}{2} \sum_{ijkl} \{ a_i^\dagger a_k^\dagger a_l a_j \}_\tau, \quad \text{(C4)} \]

and the integrals are now spin-dependent as indicated by the square brackets \([\cdots]\). Denoting the one-body portion of \( H \) by \( \{ \hat{F}_\tau \} \), is appropriate, since this term is the Fock-operator, except that the second quantized operators are normal-ordered with respect to the \( |\tau\rangle \) vacuum state, instead of the true vacuum \( |\rangle \), as in \( \hat{F}_\tau \). The two body portion of \( H \) is denoted by \( \{ r_{12}^{-1} \}_\tau \) emphasizing that this operator is determined by \( r_{12}^{-1} \) and the vacuum state \( |\tau\rangle \); furthermore, except for the shifted vacuum, the two-body portion of \( H \) is \( r_{12}^{-1} \), when this operator is expressed in second quantization.

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

\[ H = H_0 + V, \quad \text{(C5)} \]

where we require the reference state \( |\tau\rangle \) to be an eigenfunction of \( H_0 \), a one-body operator:

\[ H_0 |\tau\rangle = E_0 |\tau\rangle, \quad \text{(C6)} \]

\[ H_0 = \sum_{ij} \epsilon_{ij} a_i^\dagger a_j, \quad \text{(C7)} \]

and the zeroth-order Hamiltonian is defined by its matrix elements; we choose them by requiring the following relation to be satisfied:

\[ \epsilon_{ij} = \epsilon_{ji} = \epsilon_{ij}^\tau, \quad \text{(C8a)} \]

where

\[ \epsilon_{wr}^\tau = 0, \quad \text{(C8b)} \]

\[ \epsilon_{wx}^\tau = \langle \psi_w^\tau | \hat{f}_x^\tau | \psi_x^\tau \rangle, \quad \text{(C8c)} \]

\[ \epsilon_{rs}^\tau = \langle \psi_r^\tau | \hat{f}_u^\tau | \psi_s^\tau \rangle, \quad \text{(C8d)} \]
and the one-body operators, $\hat{f}_o^\tau$ and $\hat{f}_u^\tau$, are determined by the reference state $|\tau\rangle$, but the dependence of $\hat{f}_o^\tau$ and $\hat{f}_u^\tau$ upon $|\tau\rangle$ is at our disposal; the orbital subspaces are, again, defined by Eqs. (62) and (63).

Using the above choice, our zeroth-order Hamiltonian becomes

$$H_0^\tau = \sum_{w,x \in \{\psi_o \rightarrow \tau\}} \epsilon_{wx}^\tau a_w^\dagger a_x + \sum_{r,s \in \{\psi_u \rightarrow \tau\}} \epsilon_{rs}^\tau a_r^\dagger a_s, \quad (C9)$$

where the appended $\tau$ superscript indicates that $H_0^\tau$ now depends on the reference state $|\tau\rangle$.

A linked diagram expansion for $\chi_\tau$ and $E_{co}[\tau]$ is known to exist for a zeroth-order Hamiltonian that is a diagonal, one-body, operator [24, 29, 41, 50, 52, 53, 54, 55, 56]. A diagonal form for our one-body operator, $H_0^\tau$, is obtained when we choose its orbital sets – $\{\psi_o \rightarrow \tau\}$ and $\{\psi_u \rightarrow \tau\}$ – to satisfy the following conditions:

$$\langle \psi_{w}^{\tau} | \hat{f}_{o}^{\tau} | \psi_{x}^{\tau} \rangle = \delta_{wx}^{\tau} \epsilon_{w}^{\tau}; \quad (C10a)$$
$$\langle \psi_{r}^{\tau} | \hat{f}_{u}^{\tau} | \psi_{s}^{\tau} \rangle = \delta_{rs}^{\tau} \epsilon_{r}^{\tau}; \quad (C10b)$$

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

Using these orbitals, $H_0^\tau$ can be written as

$$H_0^\tau = \hat{O}_\tau + \hat{u}_\tau, \quad (C11)$$

where these terms – $\hat{O}_\tau$ and $\hat{u}_\tau$ – are the occupied and unoccupied portions of $H_0^\tau - (H_0^\tau)_{oc}$ and $(H_0^\tau)_{un}$ – and are given by the following:

$$\hat{O}_\tau = \sum_{w \in \{\psi_o \leftarrow \tau, \hat{f}_o^\tau\}} \epsilon_{w}^{\tau} a_w^\dagger a_w, \quad (C12a)$$
$$\hat{u}_\tau = \sum_{r \in \{\psi_u \leftarrow \tau, \hat{f}_u^\tau\}} \epsilon_{r}^{\tau} a_r^\dagger a_r, \quad (C12b)$$

where our partitioning can be written as

$$H = H_0^\tau + V_\tau. \quad (C13)$$

Using the above notation, our zeroth-order Hamiltonian in normal-ordered form can be written as

$$H_0^\tau = E_0[\tau] + \{\hat{O}_\tau\} + \hat{u}_\tau, \quad (C14)$$
where $\hat{u}_\tau$ is already normal-ordered; the constant term $E_0[\tau]$ is the zeroth-order energy of $|\tau\rangle$:

$$H_0^\tau |\tau\rangle = E_0[\tau] |\tau\rangle,$$

and is given by

$$E_0[\tau] = \sum_{\omega \in \{\psi_\omega \leftarrow \tau, \hat{f}_\tau^\dagger\}} \epsilon_{\omega}^\tau.$$  

(C15)

(C16)

Note that the first-order and the correlation energies, $E_1[\tau]$ and $E_{co}$, do not depend the zeroth-order energy $E_0[\tau]$.

The perturbation $V_\tau$, defined by Eqs. (C13), can also be written in normal-ordered form:

$$V_\tau = V_c^\tau + V_1^\tau + V_2^\tau,$$

where, from Eqs. (C1), and (C14), the individual terms are given by the following expressions:

$$V_c^\tau = E_1[\tau] - E_0[\tau],$$

(C18a)

$$V_1^\tau = \{\hat{F}_\tau\} - \{\hat{O}_\tau\} - \hat{u}_\tau,$$

(C18b)

$$V_2^\tau = \{r_{12}^{-1}\}_\tau.$$

(C18c)

The one- and two-body parts of $H$, $\{\hat{F}_\tau\}$ and $\{r_{12}^{-1}\}_\tau$, are given by Eqs. (C3) and (C4), respectively. The Goldstone diagrammatic representation of these operators can be written in the following manner 24 29 50 52 53 54 55 56:

$$\{\hat{F}_\tau\} = \bullet \ldots \text{,}$$

(C19a)

$$\{r_{12}^{-1}\}_\tau = \ldots \text{.}$$

(C19b)

The one-body part of the perturbation $V_1^\tau$ is usually represented by a single diagrammatic operator. However, for our purposes, it is convenient to use separate diagrammatic operators for the three terms on the right side of Eq. (C18b), where $\{\hat{F}_\tau\}$ is presented by Eq. (C19a). Since the other two terms are diagonal, it is appropriate to simply represent them as unfilled
arrows:

\[
-\{\hat{\Omega}_r\} = \Downarrow ,
\]

(C20a)

\[
-\hat{u}_r = \Downarrow .
\]

(C20b)

In contrast, hole- and particle-lines, by themselves, are represented by filled arrows: \(\Downarrow\) and \(\Uparrow\).

As a slight alternative to the usual approach to evaluate the diagrams of the correlation energy \(E_{\text{co}}\) and the correlation operator \(\chi_\tau\) \(\text{[5, 24, 29, 50, 52, 53, 54, 55, 56]}\), we associate an internal hole-line corresponding to a \(w\)-occupied orbital with a \(\psi_w(x_1)\psi_w^*(x_2)\) factor; we associate a particle line corresponding to an \(r\)-unoccupied orbital with a \(\psi_r(x_2)\psi_r^*(x_1)\) factor, where \(x_1\) and \(x_2\) denote the dummy integration variables that arise from the vertices. Using this convention, the sole diagram involving the Fock operator \(\hat{F}_r\) from second-order perturbation theory can be evaluated in the following manner:

\[
\begin{align*}
\begin{array}{c}
\text{\hspace{1cm}}
\end{array}
\end{align*}
= (\varepsilon_{rw}^\tau)^{-1} \int d\ x_1 \ d\ x_2 \ \left( \hat{F}_{\tau_1\tau_2}(x_1, x_2) \right) \cdot \hat{F}_{\tau_2\tau_1}(x_2, x_1),
\end{align*}
\]

(C21)

where

\[
\varepsilon_{rw}^\tau = \varepsilon_w^\tau - \varepsilon_r^\tau,
\]

(C22)

and the repeated indices \(-\ r\) and \(-\ w\) are summed over; \(\hat{F}_{\tau_i}\) denotes the Fock operator \(\hat{F}_r\) – given by Eq. (41) – acting upon \((x_i)\); the term \((\hat{F}_{\tau_i} \ldots)\) indicates that \(\hat{F}_{\tau_i}\) \textit{exclusively} acts within the brackets; furthermore, the \(w\)th component of the (one-particle) density-matrix \(\tau\) is denoted by

\[
\tau_w(x_1, x_2) = \psi_w(x_1)\psi_w^*(x_2);
\]

(C23a)

the \(r\)th orthogonal-component of \(\tau\) is denoted by

\[
\tau_r(x_1, x_2) = \psi_r(x_1)\psi_r^*(x_2),
\]

(C23b)

where, for a complete set of orbital states, we have

\[
\delta(x_1 - x_2) = \sum_w \tau_w(x_1, x_2) + \sum_r \tau_r(x_1, x_2),
\]

(C24)
which is a shorthand notations for

\[ \delta(x_1 - x_2) = \delta(r_1 - r_2)\delta_{\omega_1\omega_2}. \]  

(C25)

If we remove the top interaction from the diagram given by Eq. (C21), we see that this is a first-order diagram that contributes to the one-body portion of the correlation operator \( \chi_\tau \) [29, 38, 50]. Since the infinite-order sum of all one-body diagrams for \( \chi_\tau \) must vanish for a Bruckner orbital description, this diagram can be omitted from the expansion for the correlation energy \( E_{co} \). However, we will still consider it as a simple example to illustrate our approach and notation.

In order to further compress our notation, we use the convention that all repeated dummy indices are integrated over and restrict the Fock operator \( \hat{F}_\tau \) to exclusively act upon the first variable of any two-body function, i.e., \((\hat{F}_\tau, \alpha'(x_j, x_i)\alpha(x_i, x_j) = \alpha'(x_j, x_i)\hat{F}_\tau, \alpha(x_i, x_j))\); Eq. (C21) can then be written as

\[
\begin{align*}
\mathcal{D} &= (\varepsilon_{\tau w})^{-1} \hat{F}_{\tau_1} \tau_w(x_1, x_2) \hat{F}_{\tau_2} \tau_r(x_2, x_1), \\
\end{align*}
\]

and the other two diagrams from second-order perturbation theory have the following forms:

\[
\begin{align*}
\mathcal{D} &= \frac{1}{2}(\varepsilon_{\tau wsx})^{-1} r^{-1} r^{-1} r^{-1} \tau_w(x_1, x_3) \tau_r(x_3, x_1) \tau_s(x_2, x_4) \tau_s(x_4, x_2), \\
\mathcal{D} &= -\frac{1}{2}(\varepsilon_{\tau wsx})^{-1} r^{-1} r^{-1} r^{-1} \tau_w(x_1, x_3) \tau_r(x_3, x_2) \tau_s(x_2, x_4) \tau_s(x_4, x_1), \\
\end{align*}
\]

(C26b)

(C26c)

where

\[ \varepsilon_{\tau wsx} = \varepsilon_{\tau w} + \varepsilon_{\tau x}. \]  

(C27)

Let us also mention that when determining which dummy indices are repeated indices, it is not necessary to count indices appearing within operators. So, for example, the indices \( x_1 \) and \( x_2 \) appear twice in Eq. (C26a), and not three times, since the dummy indices from the Fock operators, i.e., \( \hat{F}_{\tau_1} \) and \( \hat{F}_{\tau_2} \), are not counted.

The diagonal terms arising from the zeroth-order Hamiltonian, given by \(-\{\hat{O}_\tau\}\) and \(-\hat{u}_\tau\), and represented by Eqs. (C20), first appear in third order. For example, the following two
diagrams can be obtained by inserting \( -\{\hat{O}_\tau\} \) and \( -\hat{u}_\tau \) into the diagram on the left side of Eq. (C26a):

\[
\begin{align*}
-\frac{(-\epsilon_w)}{\langle \varepsilon_{rw}\rangle^2} \hat{F}_{\tau_1} \tau_w(x_1, x_2) \hat{F}_{\tau_2} \tau_r(x_2, x_1), \\
-\frac{(-\epsilon_r)}{\langle \varepsilon_{rw}\rangle^2} \hat{F}_{\tau_1} \tau_w(x_1, x_2) \hat{F}_{\tau_2} \tau_r(x_2, x_1).
\end{align*}
\]

(C28a)

(C28b)

The hole-line operator \( \{\hat{O}_\tau\} \) generates an additional hole line when inserted into a diagram and, therefore, a factor of \(-1\) is included when diagram (C28a) is evaluated, where this factor cancels the \(-1\) factor from \(-\epsilon_w\). Since this type of cancellation always occurs, as an alternative, we associate a factor of \(\epsilon_w\) for \(\{\hat{O}_\tau\}\) insertions, and treat \(\{\hat{O}_\tau\}\) vertices as ones that do not generate additional hole lines; \(\hat{u}_\tau\) is associated with a \(-\epsilon_r\) factor. Keep in mind, also, that these operators generate an additional energy-denominator factor, e.g., \(\varepsilon_{rw}\), when inserted into a diagram.

The individual diagrams depend, in part, on each of the \(\tau_w\) components, given by Eq. (C23a), and the orthogonal components \(\tau_r\), given by Eq. (C23b). In addition, each diagram depends on the set of orbital energies \(\{\epsilon^r\}\), which are at our disposal. In order to make each diagram an explicit functional of the one-particle density-matrix \(\tau\), given by

\[
\tau(x_1, x_2) = \sum_w \tau_w(x_1, x_2),
\]

and its orthogonal component, \(\kappa_\tau\), given by

\[
\kappa_\tau(x_1, x_2) = \sum_r \tau_r(x_1, x_2),
\]

(C29)

(C30)

where \(\kappa_\tau\) depends, explicitly, on \(\tau\):

\[
\delta(x_1 - x_2) = \tau(x_1, x_2) + \kappa_\tau(x_1, x_2),
\]

(C31)

we choose all occupied orbitals to be degenerate, with energy \(\epsilon_o^r\); also, we choose all unoccupied orbitals to be degenerate, with energy \(\epsilon_u^r\). With these choices, the zeroth-order Hamiltonian, given by Eqs. (C11) and (C12), becomes

\[
H_0 = \epsilon_o^r \sum_{w \in \{\psi_o \leftarrow \tau, f_o^w\}} a_w^\dagger a_w + \epsilon_u^r \sum_{r \in \{\psi_u \leftarrow \tau, f_u^r\}} a_r^\dagger a_r,
\]

(C32)
and since this operator is invariant to a unitary transformation of occupied or unoccupied orbitals, it no longer depends on $\hat{f}_o^\tau$ and $\hat{f}_u^\tau$ – any set of orbitals defining $\tau$ is appropriate – so we can write

$$H_0^\tau = \epsilon_0^\tau \sum_{w \in \{\psi_o \rightarrow \tau\}} a_w^\dagger a_w + \epsilon_u^\tau \sum_{r \in \{\psi_u \rightarrow \tau\}} a_r^\dagger a_r. \quad (C33)$$

It is easily proven that all perturbative orders, except for the zeroth-order, depend on the orbital-energy difference $\varepsilon_\tau$, given by

$$\varepsilon_\tau = \epsilon_0^\tau - \epsilon_u^\tau, \quad (C34)$$

and not on the individual orbital-energies, $\epsilon_0^\tau$ and $\epsilon_u^\tau$. Therefore, we can choose ($\epsilon_u^\tau = 0$), and so our only parameter is $\varepsilon_\tau$. With this choice we have

$$H_0^\tau = \varepsilon_\tau \hat{N}_\tau, \quad (C35)$$

where $\hat{N}_\tau$ is the number operator for the occupied orbitals,

$$\hat{N}_\tau = \sum_{w \in \{\psi_o \rightarrow \tau\}} a_w^\dagger a_w, \quad (C36)$$

and it gives the total number of occupied orbitals when acting on a single determinant. In the one-particle Hilbert space, this operator is the projector for the occupied subspace – spanned by $\{\psi_o \rightarrow \tau\}$ – or, the one-particle density-matrix operator:

$$\hat{N}_\tau = \sum_{w \in \{\psi_o \rightarrow \tau\}} \langle \psi_w | \psi_w \rangle = \hat{\tau}. \quad (C37)$$

Using the above two expressions, let us generalize the definition of $\hat{\tau}$:

$$\hat{\tau} = \sum_{w \in \{\psi_o \rightarrow \tau\}} a_w^\dagger a_w, \quad (C38)$$

and write the zeroth-order Hamiltonian in a simplified form, given by

$$H_0^\tau = \varepsilon_\tau \hat{\tau}. \quad (C39)$$

By normal-ordering this expression, we have

$$H_0^\tau = \varepsilon_\tau N_\tau + \varepsilon_\tau \{\hat{\tau}\}, \quad (C40)$$
where \( N_\tau \) is the number of particles within \( |\tau\rangle \), and from Eq. (C14), we get the following identities:

\[
E_0[\tau] = \varepsilon_\tau N_\tau, \quad \text{(C41)}
\]

\[
\{\hat{O}_\tau\} = \varepsilon_\tau \{\hat{\tau}\}, \quad \text{(C42)}
\]

\[
\hat{u}_\tau = 0; \quad \text{(C43)}
\]

Furthermore, our zero- and one-body portion of the perturbation, Eqs. (C18a) and (C18b), have the following modified forms:

\[
V_\tau^c = E_1[\tau] - \varepsilon_\tau N_\tau, \quad \text{(C44a)}
\]

\[
V_\tau^1 = \{\hat{F}_\tau\} - \varepsilon_\tau \{\hat{\tau}\}. \quad \text{(C44b)}
\]

Eq. (C43) indicates that the unoccupied operator, \( \hat{u}_\tau \), represented by Eq. (C20b), does not appear in the expansion of the correlation-energy \( \mathcal{E}_{\text{co}} \); \( \{\hat{O}_\tau\} \), represented by Eq. (C20a) and given by \( \varepsilon_\tau \{\hat{\tau}\} \), is associated with a factor of \( \varepsilon_\tau \). Each diagram now becomes an explicit functional of \( \tau \) and \( \kappa_\tau \). For example, the second-order diagrams can be written in the following manner:

\[
= \varepsilon_\tau^{-1} \hat{F}_{\tau_1} \tau(\mathbf{x}_1, \mathbf{x}_2) \hat{F}_{\tau_2} \kappa_\tau(\mathbf{x}_2, \mathbf{x}_1), \quad \text{(C45)}
\]

\[
= \frac{1}{4} \varepsilon_\tau^{-1} \tau_{12}^{-1} \tau_{34}^{-1} \tau(\mathbf{x}_1, \mathbf{x}_3) \kappa_\tau(\mathbf{x}_3, \mathbf{x}_1) \tau(\mathbf{x}_2, \mathbf{x}_4) \kappa_\tau(\mathbf{x}_4, \mathbf{x}_2), \quad \text{(C46)}
\]

\[
= -\frac{1}{4} \varepsilon_\tau^{-1} \tau_{12}^{-1} \tau_{34}^{-1} \tau(\mathbf{x}_1, \mathbf{x}_3) \kappa_\tau(\mathbf{x}_3, \mathbf{x}_2) \tau(\mathbf{x}_2, \mathbf{x}_4) \kappa_\tau(\mathbf{x}_4, \mathbf{x}_1), \quad \text{(C47)}
\]

where \( \kappa_\tau \) is given by Eq. (C31). Higher order examples are presented elsewhere [30] and, in addition, a method that yields diagrams for the correlation-energy \( \mathcal{E}_{\text{co}} \) that explicitly depend on the one particle density-matrix, \( \tau \).

It is well known that the correlation operator \( \chi_\tau \) is given by a linked-diagram expansion, where all disconnected pieces are open [29, 38, 50]. Using our approach here, these diagrams
can be evaluated in an identical manner as the diagrams for the correlation energy $E_{\text{co}}$; Eq. \((\text{C}48)\) gives an example of a fifth-order one-body $\chi_r$ diagram:

\[
\varepsilon^{-1} F_{r_1 r_2}(x_1, x_2) g(x_2, x_{1'}) \psi_{r_1}'(x_{1'}) \psi_r^*(x_1) a_r^\dagger a_w, \tag{C48}
\]

where the repeated indices, $w$ and $r$, are summed over and where the two body function is given by Eq. \((\text{B}5)\). (This diagram is identical to the $(H \chi_r)_1$ diagram appearing in Eq. \((\text{B}4)\), but that diagram is evaluated slightly different, since there is no energy denominator associated with $H_r$.)

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