Application of the coupled-cluster approach to the electric dipole moment of atoms and molecules due to parity and time-reversal violation

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In this paper we present a variant of Monkhorst's coupled-cluster-based linear-response approach designed for direct calculations of static properties of closed-shell many-fermion systems [Int. J. Quantum Chem. Symp. **11**, 421 (1977)]. All the required equations are derived in the framework of the coupled-cluster singles and doubles model. Although the approach has been developed with the calculation of electric-dipole moment of atoms and molecules due to parity- and time-reversal-violating interactions in mind, it is general enough to be applicable to other problems which require the presence of two one-electron perturbations.

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I. INTRODUCTION

The possible existence of an electric-dipole moment (EDM) on an atom or a molecule, as a manifestation of parity (P) and time-reversal (T) violation in nature, has fascinated experimentalists and theorists alike for a long time [1]. Such EDM's on atoms and molecules—if they exist—are believed to be caused by P- and T-violating weak interactions among their constituents (nucleons and electrons) [2]. However, much stronger (P- and T-conserving) Coulomb forces, among the very same constituents, make the task of calculating the effects of weak interactions computationally intricate. Furthermore, calculations of EDM on heavy atoms, where the effects are more likely to be seen [3], are rather complicated because of the larger number of degrees of freedom (electrons) in such systems. A number of calculations have been performed to evaluate the EDM's of different atomic and molecular systems [4], but most of these calculations have been based on the diagrammatic many-body perturbation theory (MBPT). Even in the ordinary atomic-structure calculations employing the diagrammatic MBPT, the tremendous proliferation in the number of diagrams beyond second order remains a serious bottleneck [5]. However, if one wants to apply such an approach to the problem of atomic EDM, this proliferation is made much worse by the interplay between normal Coulomb interactions and the P- and T-violating interactions, so that bookkeeping becomes a cumbersome task, making high-precision calculations very difficult, if not impossible, to achieve [6]. In this paper we propose an alternative, nonperturbative, approach, based on the coupled-cluster method [7,8], which not only avoids the complexities of MBPT, but also achieves a clean separation of P- and T-violating interactions, from those of the dominant Coulomb forces.

The coupled-cluster method (CCM) for closed-shell systems, whose foundations were laid by Coester and Kuemmel [7,8] among others, is a nonperturbative approach to the many-body problem. This method shares the attractive property of *size extensivity* with MBPT, without the proliferation of diagrams associated with it. Size extensivity, which implies correct scaling of various extensive properties of a many-body system with its size, is of paramount importance for extended systems such as molecules. Though the CCM is an independent formalism in itself, the studies by Coester [7] and Hubbard [9] have shown that it is equivalent to summing classes of MBPT diagrams to all orders. Another strength of the CCM is its versatility, i.e., applicability to a large variety of problems in the field of many-body physics, ranging from atoms to condensed matter systems [10]. Later in this paper, we show that the evaluation of the effects of P and T violation on atomic systems amounts to the calculation of second derivatives of the energy of the system with respect to the perturbation parameters. A substantial part of the paper is concerned with developing an approach that will lead to the direct calculation of these derivatives within the coupled-cluster formalism. This approach—generally referred to as the coupled-cluster based linear-response theory (CCLRT)—is based on the philosophy outlined in the work of Monkhorst [11] and

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developed by others [12]. One of the main advantages of this approach is that we treat the external perturbation to a given order as determined by the property to be calculated. The ground state of the system is solved independently of the external perturbation where all single and double excitations are accounted for.

The remaining sections are organized as follows. In Sec. II we define the problem and establish the connection between the EDM expectation value and the energy derivatives. Then, in Sec. III, we present a brief overview of the CCM. Formulation of the CCLRT, and the derivation of all the required equations pertaining to the atomic EDM problem, is done in Sec. IV. Numerical applications of this approach to calculate the EDM's of various atomic and molecular systems, due to parity- and time-reversal-violating interactions, will be presented in future publications.

II. BACKGROUND

Here we give a brief background to the problem of P and T violation in atomic systems, and its generalization to molecules is straightforward. We assume that the unperturbed ground state of a many-electron atom is described by the eigenvalue problem

$$H_0|\psi\rangle = E|\psi\rangle \ , \tag{1}$$

where H_0 is the unperturbed Hamiltonian which is generally taken to be the Dirac-Coulomb Hamiltonian for atomic systems,

$$H_0 = \sum_i \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i mc^2 + V_{nuc}(\mathbf{r}_i)\right] + \sum_{\substack{i,j \\ j<i}} \frac{e^2}{r_{ij}} \ . \tag{2}$$

The two-electron part of this Hamiltonian is not Lorentz invariant. One could add the Breit interaction [13] to the Hamiltonian as a correction. It is also important to use a relativistic many-body approach which avoids the continuum dissolution problem associated with the negative energy solutions that one encounters while using the Hamiltonian of Eq. (2) [14]. One such approach is the so-called no pair approximation of Sucher whereby one projects out all the negative energy solutions from the model space [15]. However, the CCLRT formalism that we develop later is independent of the details of the relativistic nature of the problem, and is equally applicable to a nonrelativistic situation, where H_0 would be the Schrödinger many-body Hamiltonian. The many-electron state $|\psi\rangle$, which is also an eigenstate of total angular momentum and parity, will, in general, be a linear combination of Slater determinants composed of one-electron states. If one were to choose H_0 of Eq. (2), these one-electron states will be four-component Dirac spinors.

However, if the parity- and time-reversal symmetries were being broken by an interaction gH_{PTV}, then, in the presence of an external electric field E (in the z direction), the total atomic Hamiltonian will be

$$H = H_0 - \sum_i ez_i E + gH_{PTV} \ , \tag{3}$$

where $\sum_i ez_i$ is the electric-dipole operator of the atom, g is a parameter determining the strength of P- and T-violating interaction H_{PTV}, and the subscript PTV refers to the violation of parity- and time-reversal symmetries. The explicit forms of g and H_{PTV} will be determined by the mechanism leading to P and T violation. For example, to study P and T violation caused by an intrinsic EDM on an electron, one can take as perturbation [16]

$$H_{int} = 2icd_e \sum_i \beta_i \gamma_{5i} \mathbf{p}_i^2, \tag{4}$$

where d_e is the intrinsic EDM of electron, β and γ_5 are the Dirac matrices, the subscript i runs over the electrons in the system, and $\mathbf{p}_i$ is the momentum of the ith electron. Since the unknown parameter d_e determines the strength of the interaction H_{int}, the obvious choice for g and H_{PTV} in this case will be

$$\begin{aligned} g &= d_e, \\ H_{PTV} &= 2ic \sum_i \beta_i \gamma_{5i} \mathbf{p}_i^2 \ . \end{aligned} \tag{5}$$

If the atom has a permanent EDM, there will be a shift in its energy when it is acted on by an electric field. If the applied field is sufficiently weak, the shift in the energy will be linear with respect to the field strength. If the change in the energy is W^E, the electric dipole moment of the atom is defined as

$$D = \lim_{E\to 0} \left(-\frac{\partial W^E}{\partial E} \right) \ . \tag{6}$$

Clearly, the first nonvanishing contribution to the energy shift which is linear in the strength of the external electric field, is obtained in the second order of the perturbation theory,

$$W^E = \sum_{\psi_e \neq \psi} \frac{\langle\psi|gH_{PTV}|\psi_e\rangle\langle\psi_e| - \sum_i ez_i E|\psi\rangle}{E_\psi - E_{\psi_e}} + \text{c.c.} \tag{7}$$

Here E_{ψ_e}'s are the energies corresponding to the intermediate states $|\psi_e\rangle$, and E_ψ is the energy of the state $|\psi\rangle$. Clearly, for W^E to be nonzero, the parities of the states $|\psi_e\rangle$ have to be opposite to that of the unperturbed state $|\psi\rangle$. Using Eq. (6), we get the expression for the EDM of the atom,

$$D = \sum_{\psi_e} \frac{\langle\psi|gH_{PTV}|\psi_e\rangle\langle\psi_e|\sum_i ez_i|\psi\rangle}{E_\psi - E_{\psi_e}} + \text{c.c.} \tag{8}$$

Since the perturbation parameter g, in general, is an unknown quantity (such as d_e above), the quantity that one calculates is the ratio [17],

$$R = \frac{D}{g}. \tag{9}$$

It is easy to conclude from Eqs. (6), (8), and (9) that

$$R = -\left.\frac{\partial^2 W^E}{\partial g \partial E}\right|_{E=0\,;\,g=0} . \tag{10}$$

It is this relationship between the second derivative of energy and the ratio R which will be utilized in the direct evaluation of the latter by means of the CCM. In the following section we give a brief outline of the CCM.

III. THE COUPLED-CLUSTER METHOD

According to the original proposal of Coester [7], the exact wave function $|\psi\rangle$ of a closed-shell many-fermion system can be written as

$$|\psi\rangle = e^T|\phi_0\rangle\ , \tag{11}$$

where T is the *cluster operator* and $|\phi_0\rangle$ is an independent particle (i.e., uncorrelated) reference state function. For example, $|\phi_0\rangle$ could be a Slater determinant composed of Hartree-Fock single-particle states. The cluster operator T is defined as

$$T = \sum_{l=1}^{N} T_l\ , \tag{12}$$

where N is the total number of fermions in the system.

The individual cluster operators T_l are defined in terms of second-quantized operators as

$$\begin{aligned} T_1 &= \sum_{i,a} t_i^a \{a_a^+ a_i\}, \\ T_2 &= \sum_{\substack{a>b \\ i>j}} t_{ij}^{ab} \{a_a^+ a_i a_b^+ a_j\}, \\ &\vdots \\ T_l &= \sum_{\substack{a>b>c\cdots \\ i>j>k\cdots}} t_{ijk\cdots}^{abc\cdots} \{a_a^+ a_i a_b^+ a_j a_c^+ a_k \ldots\}, \\ &\vdots\ . \end{aligned} \tag{13}$$

In the convention we have adopted, subscripts (superscripts) $i, j, k, \ldots (a, b, c, \ldots)$ refer to the orbitals which are occupied (unoccupied) in the reference state function $|\phi_0\rangle$. Curly brackets, $\{\ldots\}$, around a group of creation and annihilation operators imply normal ordering. Cluster coefficients like t_{ij}^{ab} are fully antisymmetrized, i.e.,

$$\begin{aligned} t_{ij}^{ab} &= -t_{ji}^{ab} = -t_{ij}^{ba} = \cdots, \\ t_{ijk}^{abc} &= -t_{jik}^{abc} = -t_{ijk}^{bac} = \cdots, \\ &\vdots\ . \end{aligned} \tag{14}$$

If H is the Hamiltonian of the system and E is the exact energy, we have

$$H|\psi\rangle = E|\psi\rangle\ . \tag{15}$$

If we multiply both sides of Eq. (15) with e^{-T} and use Eq. (11) we get

$$e^{-T} H e^T |\phi_0\rangle = E|\phi_0\rangle. \tag{16}$$

On projecting Eq. (16) onto the space of the state functions $\{|\phi_0\rangle, |\phi_i^a\rangle, |\phi_{ij}^{ab}\rangle, \ldots, |\phi_{ijk\ldots}^{abc\ldots}\rangle, \ldots\}$, one gets

$$\langle\phi_0|e^{-T} H e^T|\phi_0\rangle = E \tag{17}$$

and

$$\begin{aligned} \langle\phi_i^a|e^{-T} H e^T|\phi_0\rangle &= 0, \\ \langle\phi_{ij}^{ab}|e^{-T} H e^T|\phi_0\rangle &= 0, \\ &\vdots \\ \langle\phi_{ijk\ldots}^{abc\ldots}|e^{-T} H e^T|\phi_0\rangle &= 0, \\ &\vdots\ . \end{aligned} \tag{18}$$

In the equations above $|\phi_{ijk\ldots}^{abc\ldots}\rangle$ denotes a general n-fold excited determinant obtained by exciting(deexciting) n-fermions out of the occupied states (holes) $i, j, k, \ldots$ into the unoccupied states (particles) $a, b, c, \ldots$. Equations (18) are a set of coupled nonlinear equations which can be solved to get the cluster coefficients $\{t_i^a, t_{ij}^{ab}, \ldots, t_{ijk\ldots}^{abc\ldots}, \ldots\}$, thus determining the exact wave function $|\psi\rangle$. These cluster coefficients can then be substituted in Eq. (17) to evaluate E.

Full solution of the coupled-cluster equations for an N-fermion system would entail solving Eqs. (18) for all possible N-fold excitations out of the reference state function $|\phi_0\rangle$. This becomes highly impractical even for relatively small values of N. Therefore, practical applications of CCM mandate that we truncate the cluster expansion of Eq. (12) to small values of N. One such possibility is the so-called coupled-cluster singles and doubles approximation (CCSD) [18,19] which truncates Eq. (12) at $l = 2$, i.e.,

$$T = T_1 + T_2\ . \tag{19}$$

Therefore, in order to determine the cluster coefficients for the CCSD approximation, the nonlinear equations one has to solve are

$$\begin{aligned} \langle\phi_i^a|e^{-T} H e^T|\phi_0\rangle &= 0, \\ \langle\phi_{ij}^{ab}|e^{-T} H e^T|\phi_0\rangle &= 0\ . \end{aligned} \tag{20}$$

The solutions of T can be substituted in Eq. (17) to get the value of the energy E. The detailed expressions for

nonlinear equations represented by Eqs. (20) have been derived by Cullen and Zerner [19] using a diagrammatic approach.

IV. COUPLED-CLUSTER-BASED LINEAR-RESPONSE METHOD

If we were to apply the traditional CCM to the problem of atomic EDM by simply adding a parity- and time-reversal-violating Hamiltonian H_{PTV} to the atomic many-body Hamiltonian, it will amount to treating H_{PTV} to all orders along with the electron correlation. The unknown parameters associated with H_{PTV} can lead to numerical problems while solving the coupled-cluster equations. To circumvent this, we formulate the atomic EDM problem using the coupled-cluster based linear-response theory, as outlined by Monkhorst [11].

Basic formalism

The basic philosophy behind the coupled-cluster-based linear-response approach is to treat the P- and T-violating term H_{PTV} of the atomic many-body Hamiltonian only to first order, while treating the electron correlation to all orders. The other significant advantage of this approach is that it leads to direct calculation of the expectation value of an operator (in our case, to be more precise, the energy derivatives), instead of the usual way of first calculating the wave function and then finding the expectation value. Following Monkhorst's approach we consider the perturbed Hamiltonian to be

$$H(g_1,g_2) = H + g_1 O_1 + g_2 O_2 \ , \tag{21}$$

where H is the atomic many-body Hamiltonian, g_1 and g_2 are the perturbation parameters associated with the perturbation operators O_1 and O_2. By comparing Eqs. (21) and (3), the natural choices for g_1, O_1, g_2, and O_2, for the problem of calculating EDM of an atom due to P and T violation, will be

$$\begin{aligned} g_1 &= -E, \\ O_1 &= D \ , \end{aligned} \tag{22}$$

and

$$\begin{aligned} g_2 &= g, \\ O_2 &= H_{PTV} \ , \end{aligned} \tag{23}$$

where the explicit forms of g and H_{PTV} depend on the mechanism responsible for P and T violation in the atom. However, we must emphasize that our exposition of CCLRT is *quite general* in that it can be easily applied to any other case of interest where the problem can be formulated as a double perturbation problem.

With the new Hamiltonian of Eq. (21), Eq. (16) can be generalized to

$$e^{-T(g_1,g_2)} H(g_1,g_2) e^{T(g_1,g_2)} |\phi_0\rangle = E(g_1,g_2)|\phi_0\rangle \ . \tag{24}$$

Therefore, the counterparts of Eqs. (17) and (18) will be

$$\langle\phi_0| e^{-T(g_1,g_2)} H(g_1,g_2) e^{T(g_1,g_2)} |\phi_0\rangle = E(g_1,g_2) \tag{25}$$

and

$$\langle\phi^{ab\cdots}_{ij\cdots}| e^{-T(g_1,g_2)} H(g_1,g_2) e^{T(g_1,g_2)} |\phi_0\rangle = 0 \ . \tag{26}$$

If the coefficients g_1 and g_2 are small, the new energy $E(g_1,g_2)$ and the new cluster operator $T(g_1,g_2)$, can be Taylor expanded in terms of them, i.e.,

$$\begin{aligned} E(g_1,g_2) &= E + g_1 E^{(1,0)} + g_2 E^{(0,1)} + g_1 g_2 E^{(1,1)} + \cdots , \\ T(g_1,g_2) &= T + g_1 T^{(1,0)} + g_2 T^{(0,1)} + g_1 g_2 T^{(1,1)} + \cdots \ . \end{aligned} \tag{27}$$

From Eq. (27) above, it is clear

$$E^{(1,1)} = \left.\frac{\partial^2}{\partial g_1 \partial g_2} E(g_1,g_2)\right|_{g_1=0\ ;\ g_2=0} \ . \tag{28}$$

However, by looking at the definition of ratio R in Eq. (10), it is obvious that if one were to define g_1, g_2, O_1, and O_2 according to Eqs. (22) and (23),

$$R = E^{(1,1)} \ . \tag{29}$$

Therefore, the quantity of interest for the atomic EDM problem is $E^{(1,1)}$. Now we will derive the expressions for $E^{(1,1)}$, and the equations determining the associated cluster operators. In order to do that, first we substitute the quantities from Eq. (27) in Eq. (24),

$$\left(E + g_1 E^{(1,0)} + g_2 E^{(0,1)} + g_1 g_2 E^{(1,1)} + \cdots\right) |\phi_0\rangle$$
$$= e^{-T} \left(e^{-g_1 T^{(1,0)}} e^{-g_2 T^{(0,1)}} e^{-g_1 g_2 T^{(1,1)}}\right) (H + g_1 O_1 + g_2 O_2) \left(e^{g_1 T^{(1,0)}} e^{g_2 T^{(0,1)}} e^{g_1 g_2 T^{(1,1)}}\right) e^{T} |\phi_0\rangle \ .$$

Since we are interested in expressing both the sides of the equation above in terms of various powers of the coefficients g_1 and g_2, we expand the exponential terms like $e^{g_1 T^{(1,0)}}$ to get

$$\left(E + g_1 E^{(1,0)} + g_2 E^{(0,1)} + g_1 g_2 E^{(1,1)} + \cdots\right) |\phi_0\rangle$$
$$= e^{-T} \left[(1 - g_1 T^{(1,0)} + \cdots)(1 - g_2 T^{(0,1)} + \cdots)(1 - g_1 g_2 T^{(1,1)} + \cdots)\right]$$
$$\times (H + g_1 O_1 + g_2 O_2) \left[(1 + g_1 T^{(1,0)} + \cdots)(1 + g_2 T^{(0,1)} + \cdots)(1 + g_1 g_2 T^{(1,1)} + \cdots)\right] e^{T} |\phi_0\rangle \ .$$

Comparing the terms independent of g_1 and g_2 on both sides of the above expression, not too surprisingly, gives us the unperturbed coupled-cluster equation

$$e^{-T}He^{T}|\phi_0\rangle = E|\phi_0\rangle \ .$$

From the terms proportional to g_1, after a little algebra, we get the following equation which determines the cluster operator $T^{(1,0)}$ and $E^{(1,0)}$:

$$e^{-T}\left(O_1 + [H, T^{(1,0)}]\right) e^{T}|\phi_0\rangle = E^{(1,0)}|\phi_0\rangle \ , \qquad (30)$$

where square brackets $[\ldots]$ denote a commutator; i.e., for operators A and B, $[A,B] = AB - BA$. Above, terms proportional to g_2 give us the equation which determines $T^{(0,1)}$ and $E^{(0,1)}$,

$$e^{-T}\left(O_2 + [H, T^{(0,1)}]\right) e^{T}|\phi_0\rangle = E^{(0,1)}|\phi_0\rangle \ . \qquad (31)$$

Finally, the terms proportional to $g_1 g_2$ give us the equations determining $E^{(1,1)}$ and $T^{(1,1)}$,

$$e^{-T}\Bigg([O_1, T^{(0,1)}] + [O_2, T^{(1,0)}] + [H, T^{(1,1)}] + \Big[[H, T^{(1,0)}], T^{(0,1)}\Big]\Bigg) e^{T}|\phi_0\rangle = E^{(1,1)}|\phi_0\rangle \ . \qquad (32)$$

By projecting Eqs. (30)–(32) onto the space of the functions $\{|\phi_0\rangle, |\phi_i^a\rangle, |\phi_{ij}^{ab}\rangle, \ldots, |\phi_{ijk\ldots}^{abc\ldots}\rangle, \ldots\}$, and using the fact that various cluster operators commute with each other, we get the equations determining $T^{(0,1)}$, $T^{(1,0)}$, $T^{(1,1)}$, and $E^{(1,1)}$,

$$\langle\phi_{ij\ldots}^{ab\ldots}|\left(\bar{O}_1 + [\bar{H}, T^{(1,0)}]\right)|\phi_0\rangle = 0 \ , \qquad (33)$$

and

$$\langle\phi_{ij\ldots}^{ab\ldots}|\left(\bar{O}_2 + [\bar{H}, T^{(0,1)}]\right)|\phi_0\rangle = 0 \ , \qquad (34)$$

and

$$\langle\phi_{ij\ldots}^{ab\ldots}|([\bar{O}_1, T^{(0,1)}] + [\bar{O}_2, T^{(1,0)}] + [\bar{H}, T^{(1,1)}] + [[\bar{H}, T^{(1,0)}], T^{(0,1)}])|\phi_0\rangle = 0 \ , \qquad (35)$$

and

$$E^{(1,1)} = \langle\phi_0|([\bar{O}_1, T^{(0,1)}] + [\bar{O}_2, T^{(1,0)}] + [\bar{H}, T^{(1,1)}] + [[\bar{H}, T^{(1,0)}], T^{(0,1)}])|\phi_0\rangle \ , \qquad (36)$$

where, for the sake of brevity, for any general operator O, we have used the expression $\bar{O} = e^{-T}Oe^{T}$. Since both the operators O_1 and O_2 represent one body interactions, they can be expressed as

$$O_1 = \sum_{p,q} d_{pq} a_p^{+} a_q,$$
$$O_2 = \sum_{p,q} h'_{pq} a_p^{+} a_q \ , \qquad (37)$$

where d_{pq} and h'_{pq} are, respectively, the matrix elements of the operators O_1 and O_2 over single particle states labeled p and q. Cluster operators such as $T^{(1,0)}$ can themselves be expanded as

$$T^{(1,0)} = \sum_{l=1}^{N} T_l^{(1,0)},$$
$$T^{(0,1)} = \sum_{l=1}^{N} T_l^{(0,1)},$$
$$T^{(1,1)} = \sum_{l=1}^{N} T_l^{(1,1)} \ ,$$

where

$$T_1^{(1,0)} = \sum_{\substack{a \\ i}} {}^{(1,0)}t_i^a \{a_a^{+} a_i\},$$
$$T_2^{(1,0)} = \sum_{\substack{a>b \\ i>j}} {}^{(1,0)}t_{ij}^{ab} \{a_a^{+} a_i a_b^{+} a_j\}, \qquad (38)$$

However, keeping practical applications in mind, we truncate the expansions of $T^{(1,0)}$, $T^{(0,1)}$, and $T^{(1,1)}$ to, at the most, double excitations; i.e.,

$$T^{(1,0)} = T_1^{(1,0)} + T_2^{(1,0)},$$
$$T^{(0,1)} = T_1^{(0,1)} + T_2^{(0,1)},$$
$$T^{(1,1)} = T_1^{(1,1)} + T_2^{(1,1)} \ . \qquad (39)$$

As a result of this approximation, the equations determining cluster operators $T^{(1,0)}$, $T^{(0,1)}$, and $T^{(1,1)}$, and the energy derivative $E^{(1,1)}$, become

$$\langle\phi_i^a|\left(\bar{O}_1 + \{\bar{H}_N T^{(1,0)}\}_C\right)|\phi_0\rangle = 0,$$
$$\langle\phi_{ij}^{ab}|\left(\bar{O}_1 + \{\bar{H}_N T^{(1,0)}\}_C\right)|\phi_0\rangle = 0 \ , \qquad (40)$$

and

$$\langle\phi_i^a|\left(\bar{O}_2 + \{\bar{H}_N T^{(0,1)}\}_C\right)|\phi_0\rangle = 0,$$
$$\langle\phi_{ij}^{ab}|\left(\bar{O}_2 + \{\bar{H}_N T^{(0,1)}\}_C\right)|\phi_0\rangle = 0 \ , \qquad (41)$$

and

$$\langle\phi_i^a|(\{\bar{O}_1 T^{(0,1)}\}_C + \{\bar{O}_2 T^{(1,0)}\}_C + \{\bar{H}_N T^{(1,1)}\}_C + \{\bar{H}_N T^{(1,0)} T^{(0,1)}\}_C)|\phi_0\rangle = 0, \qquad (42)$$

$$\langle\phi_{ij}^{ab}|\left(\{\bar{O}_1 T^{(0,1)}\}_C + \{\bar{O}_2 T^{(1,0)}\}_C + \{\bar{H}_N T^{(1,1)}\}_C + \{\bar{H}_N T^{(1,0)} T^{(0,1)}\}_C\right)|\phi_0\rangle = 0 \ .$$

and

$$E^{(1,1)} = \langle\phi_0| \left(\{\bar{O}_1 T^{(0,1)}\}_C + \{\bar{O}_2 T^{(1,0)}\}_C + \{\bar{H}_N T^{(1,1)}\}_C + \{\bar{H}_N T^{(1,0)} T^{(0,1)}\}_C \right) |\phi_0\rangle \, . \tag{43}$$

Above $\bar{H}_N$ implies the normal-ordered form of the operator $\bar{H} = e^{-T} H e^{T}$, and the subscript C implies that there is at least one contraction among the creation (annihilation) operators of $\bar{H}_N$ and annihilation (creation) operators of cluster operators, leading to connected diagrams in the diagrammatic approach [5]. We have also used the Wick's theorem [20] and the linked-cluster theorem [21] to reduce the commutators of Eqs. (33)–(36) to get the connected products of normal-ordered terms above in Eqs. (40)–(43). These steps are given in more detail in Ref. [22].

By applying the rules of diagrammatic coupled-cluster theory [5] to various terms of the expansions illustrated above, one can finally get the detailed mathematical expressions, in terms of various cluster amplitudes and the Hamiltonian matrix elements, for all the CCLRT equations for $T^{(1,0)}$, $T^{(0,1)}$, and $T^{(1,1)}$. The equations are rather lengthy and have been relegated to the Appendix.

It is clear from the cluster amplitude equations given in the Appendix that ${}^{(1,0)}t_i^a$, ${}^{(0,1)}t_{ij}^{ab}$, ${}^{(1,1)}t_{ij}^{ab}$, ... satisfy linear equations unlike the cluster amplitudes $t_i^a, t_{ij}^{ab}, \ldots$. However, to solve for ${}^{(1,0)}t_i^a$, ${}^{(0,1)}t_{ij}^{ab}$, ${}^{(1,1)}t_{ij}^{ab}, \ldots$, we do need the complete solutions for $t_i^a, t_{ij}^{ab}, \ldots$, as is quite clear from those equations. Therefore, in CCLRT, one first solves for the unperturbed problem and determines the T operators. Those solutions of T are then substituted in Eqs. (A1)–(A4), which are then solved to get the cluster coefficients corresponding to $T^{(1,0)}$, $T^{(0,1)}$, and $T^{(1,1)}$, thus completing the solution.

V. DISCUSSION

In this paper we have presented a variant of Monkhorst's [11] coupled-cluster approach particularly suited for—but not limited to—the calculation of the atomic EDM due to parity- and time-reversal-violating interactions. This approach is fully linked, and, therefore, it also allows for the calculation of properties of extended systems such as molecules and clusters. The properties to be calculated depend on cluster coefficients whose solution is a mathematical problem formulated independent of the calculation of the correlated ground state of the system. The cluster coefficients needed for calculating the properties of interest are solutions of linear equations which should not be difficult to solve provided one has a good solution to the ground state problem. In the future we plan to implement this approach numerically to test the viability of the approach.

APPENDIX A: THE EXPRESSIONS FOR CCLRT EQUATIONS FOR $T^{(1,0)}$, $T^{(0,1)}$, AND $T^{(1,1)}$ AMPLITUDES

The detailed diagrammatic derivation of the equations satisfied by various cluster amplitudes is given in Ref. [22]. Since this derivation is quite lengthy, consisting of a large number of diagrams, here we just quote the final results. The linear equations which determine the cluster coefficients ${}^{(1,0)}t_i^a$ and ${}^{(1,0)}t_{ij}^{ab}$ are found to be

$$\begin{aligned}
&\langle\phi_i^a| \left(\bar{O}_1 + \{\bar{H}_N T^{(1,0)}\}_C \right) |\phi_0\rangle \\
&= d_{ai} + \sum_c d_{ac} t_i^c - \sum_k d_{ki} t_k^a + \sum_{c,k} d_{kc} (t_{ki}^{ca} - t_i^c t_k^a) + \sum_c f_{ac}\, {}^{(1,0)}t_i^c \\
&+ \sum_{k,c} f_{kc} ({}^{(1,0)}t_{ik}^{ac} - {}^{(1,0)}t_i^c t_k^a - {}^{(1,0)}t_k^a t_i^c) - \sum_k f_{ki}\, {}^{(1,0)}t_k^a - \sum_{c,k} \langle k\, a || i\, c\rangle\, {}^{(1,0)}t_k^c \\
&+ \sum_{c,d,k} \langle a\, k || d\, c\rangle \left(\frac{1}{2}\, {}^{(1,0)}t_{ik}^{dc} + {}^{(1,0)}t_i^d t_k^c + {}^{(1,0)}t_k^c t_i^d \right) - \sum_{c,k,l,d} \langle k\, l || c\, d\rangle \left(\frac{1}{2}\, {}^{(1,0)}t_i^c t_{kl}^{ad} \right. \\
&\left. + {}^{(1,0)}t_i^c t_k^a t_l^d + \frac{1}{2}\, {}^{(1,0)}t_k^a t_{il}^{cd} + {}^{(1,0)}t_k^a t_i^c t_l^d - {}^{(1,0)}t_k^d t_i^c t_l^a - {}^{(1,0)}t_k^c t_{li}^{da} - {}^{(1,0)}t_{ik}^{ac} t_l^d \right. \\
&\left. + \frac{1}{2}\, {}^{(1,0)}t_{il}^{cd} t_k^a + \frac{1}{2}\, {}^{(1,0)}t_{kl}^{ad} t_i^c \right) - \sum_{c,k,l} \langle l\, k || i\, c\rangle \left({}^{(1,0)}t_l^a t_k^c + {}^{(1,0)}t_k^c t_l^a + \frac{1}{2}\, {}^{(1,0)}t_{lk}^{ac} \right) = 0 \, ,
\end{aligned} \tag{A1}$$

and

$$
\begin{aligned}
&\langle \phi_{ij}^{ab}| \left(\bar{O}_1 + \{ \bar{H}_N T^{(1,0)} \}_C \right) |\phi_0\rangle \\
&= \sum_p (-1)^p P(ab) \sum_c d_{bc} t_{ij}^{ac} - \sum_p (-1)^p P(ij) \sum_k d_{kj} t_{ik}^{ab} - \sum_p (-1)^p P(ij) \sum_{c,k} d_{kc} t_j^c t_{ik}^{ab} \\
&- \sum_p (-1)^p P(ab) \sum_{c,k} d_{kc} t_k^b t_{ij}^{ac} + \sum_p (-1)^p P(ab) \sum_c f_{bc}{}^{(1,0)} t_{ij}^{ac} \\
&+ \sum_p (-1)^p P(ab) \sum_{c,k,d} \langle k\, b || c\, d \rangle t_k^c{}^{(1,0)} t_{ij}^{ad} - \sum_p (-1)^p P(ab) \sum_{k,c} f_{kc} t_k^b{}^{(1,0)} t_{ij}^{ac} \\
&- \frac{1}{2} \sum_p (-1)^p P(ab) \sum_{c,k,l,d} \langle k\, l || c\, d \rangle \left(t_{kl}^{cb} + 2 t_k^c t_l^b \right)^{(1,0)} t_{ij}^{ad} \\
&- \sum_p (-1)^p P(ij) \sum_k f_{kj}{}^{(1,0)} t_{ik}^{ab} - \sum_p (-1)^p P(ij) \sum_{c,k} f_{kc} t_j^c{}^{(1,0)} t_{ik}^{ab} \\
&+ \sum_p (-1)^p P(ij) \sum_{c,k,l} \langle k\, l || c\, j \rangle t_k^c{}^{(1,0)} t_{il}^{ab} \\
&- \frac{1}{2} \sum_p (-1)^p P(ij) \sum_{ckld} \langle k\, l || c\, d \rangle^{(1,0)} t_{il}^{ab} \left(t_{kj}^{cd} + 2 t_k^c t_j^d \right) \\
&+ \sum_p (-1)^p P(ij) \sum_c \langle a\, b || i\, c \rangle^{(1,0)} t_j^c + \sum_p (-1)^p P(ij) \sum_{c,d} \langle a\, b || c\, d \rangle^{(1,0)} t_i^c t_j^d \\
&- \sum_p (-1)^p P(ij|ab) \sum_{c,k} \langle k\, a || c\, i \rangle^{(1,0)} t_j^c t_k^b - \sum_p (-1)^p P(ij) \sum_{c,k} f_{kc}{}^{(1,0)} t_j^c t_{ik}^{ab} \\
&- \sum_p (-1)^p P(ij|ab) \sum_{c,d,k} \langle k\, b || c\, d \rangle^{(1,0)} t_j^c \left(t_k^a t_i^d + t_{ki}^{ad} \right) \\
&+ \frac{1}{2} \sum_p (-1)^p P(ij) \sum_{c,k,l} \langle k\, l || c\, j \rangle^{(1,0)} t_i^c \left(t_{kl}^{ab} + t_k^a t_l^b \right) \\
&- \sum_p (-1)^p P(ij) \sum_{c,k,l,d} \langle k\, l || c\, d \rangle^{(1,0)} t_i^c \left(t_k^a t_{lj}^{db} - t_k^b t_{lj}^{da} + t_l^d t_{kj}^{ab} \right) \\
&+ \frac{1}{2} \sum_p (-1)^p P(ij) \langle kl || cd \rangle^{(1,0)} t_i^c t_j^d \left(t_{kl}^{ab} + t_k^a t_l^b \right) \\
&- \sum_p (-1)^p P(ab) \sum_k \langle k\, a || j\, i \rangle^{(1,0)} t_k^b + \sum_p (-1)^p P(ab) \sum_{k,l} \langle k\, l || i\, j \rangle^{(1,0)} t_k^a t_l^b \\
&- \sum_p (-1)^p P(ij|ab) \sum_{c,k} \langle k\, a || c\, i \rangle^{(1,0)} t_k^b t_j^c - \sum_p (-1)^p P(ab) \sum_{k,c} f_{kc}{}^{(1,0)} t_k^b t_{ij}^{ac} \\
&+ \sum_p (-1)^p P(ij|ab) \sum_{k,c,l} \langle l\, k || c\, j \rangle^{(1,0)} t_l^b \left(t_{ik}^{ca} + t_i^c t_k^a \right) \\
&- \frac{1}{2} \sum_p (-1)^p P(ab) \sum_{l,c,d} \langle l\, a || c\, d \rangle^{(1,0)} t_l^b \left(t_{ij}^{cd} + t_i^c t_j^d \right) \\
&- \sum_p (-1)^p P(ab) \sum_{c,k,l,d} \langle k\, l || c\, d \rangle^{(1,0)} t_k^b \left(t_j^c t_{il}^{ad} - t_i^c t_{jl}^{ad} + t_l^d t_{ij}^{ac} \right) \\
&+ \frac{1}{2} \sum_p (-1)^p P(ab) \sum_{c,k,l,d} \langle k\, l || c\, d \rangle^{(1,0)} t_l^b t_k^a \left(t_{ij}^{cd} + t_i^c t_j^d \right) \\
&+ \frac{1}{2} \sum_{c,d} \langle a\, b || c\, d \rangle^{(1,0)} t_{ij}^{cd} - \frac{1}{2} \sum_p (-1)^p P(ab) \sum_{c,d,k} \langle a\, k || c\, d \rangle^{(1,0)} t_{ij}^{cd} t_k^b \\
&+ \frac{1}{4} \sum_{c,d,k,l} \langle k\, l || c\, d \rangle^{(1,0)} t_{ij}^{cd} \left(t_{kl}^{ab} + t_k^a t_l^b \right) + \frac{1}{2} \sum_k \langle k\, l || i\, j \rangle^{(1,0)} t_{kl}^{ab} \\
&+ \frac{1}{2} \sum_p (-1)^p P(ij) \sum_{c,k,l} \langle k\, l || i\, c \rangle^{(1,0)} t_{kl}^{ab} t_j^c + \frac{1}{4} \sum_{c,d,k,l} \langle k\, l || c\, d \rangle^{(1,0)} t_{kl}^{ab} \left(t_{ij}^{cd} + t_i^c t_j^d \right) \\
&- \sum_p (-1)^p P(ij|ab) \sum_{c,k} \langle a\, k || c\, i \rangle^{(1,0)} t_{jk}^{cb} - \sum_p (-1)^p P(ij|ab) \sum_{c,k,d} \langle a\, k || c\, d \rangle^{(1,0)} t_{ik}^{cb} t_j^d
\end{aligned}
$$

$$
\begin{aligned}
&+\sum_p(-1)^p P(ij|ab)\sum_{k,l,c}\langle k\,l||i\,c\rangle^{(1,0)}t^{ac}_{kj}t^b_l-\sum_p(-1)^p P(ij|ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle^{(1,0)}t^{ac}_{ik}\left(t^{db}_{jl}+t^d_jt^b_l\right)\\
&+\sum_p(-1)^p P(ab)\sum_{c,k,d}\langle k\,b||c\,d\rangle^{(1,0)}t^c_kt^{ad}_{ij}-\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\,l||c\,j\rangle^{(1,0)}t^c_kt^{ab}_{il}\\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle^{(1,0)}t^c_kt^d_jt^{ab}_{il}-\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle^{(1,0)}t^c_kt^b_lt^{ad}_{ij}\\
&-\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle^{(1,0)}t^{cd}_{kj}t^{ab}_{il}-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle^{(1,0)}t^{cb}_{kl}t^{ad}_{ij}=0\,. \qquad \text{(A2)}
\end{aligned}
$$

Because of the identical structure of equations satisfied by cluster operators $T^{(1,0)}$and, $T^{(0,1)}$ [compare Eqs. (40) and (41)], we can get the equations determining $T^{(0,1)}$ by replacing the amplitudes ${}^{(1,0)}t^a_i$ and ${}^{(1,0)}t^{ab}_{ij}$ by ${}^{(0,1)}t^a_i$ and ${}^{(0,1)}t^{ab}_{ij}$, and d_{ij} by h'_{ij} in Eq. (A2) above. Equations which determine ${}^{(1,1)}t^a_i$ and ${}^{(1,1)}t^{ab}_{ij}$ are

$$
\begin{aligned}
&\langle\phi^a_i|\left(\{\bar{H}_NT^{(1,1)}\}_C+\{\bar{O}_1T^{(0,1)}\}_C+\{\bar{O}_2T^{(1,0)}\}_C+\{\bar{H}_NT^{(1,0)}T^{(0,1)}\}_C\right)|\phi_0\rangle\\
&=\sum_c f_{ac}\,{}^{(1,1)}t^c_i+\sum_{k,c}f_{kc}({}^{(1,1)}t^{ac}_{ik}-{}^{(1,1)}t^c_it^a_k-{}^{(1,1)}t^a_kt^c_i)-\sum_k f_{ki}\,{}^{(1,1)}t^a_k\\
&-\sum_{c,k}\langle k\,a||i\,c\rangle\,{}^{(1,1)}t^c_k+\sum_{c,d,k}\langle a\,k||d\,c\rangle\left(\frac{1}{2}{}^{(1,1)}t^{dc}_{ik}+{}^{(1,1)}t^d_it^c_k+{}^{(1,1)}t^c_kt^d_i\right)\\
&-\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\left(\frac{1}{2}{}^{(1,1)}t^c_it^{ad}_{kl}+{}^{(1,1)}t^c_it^a_kt^d_l+\frac{1}{2}{}^{(1,1)}t^a_kt^{cd}_{il}+{}^{(1,1)}t^a_kt^c_it^d_l-{}^{(1,1)}t^d_kt^c_it^a_l\right.\\
&\left.-{}^{(1,1)}t^c_kt^{da}_{li}-{}^{(1,1)}t^{ac}_{ik}t^d_l+\frac{1}{2}{}^{(1,1)}t^{cd}_{il}t^a_k+\frac{1}{2}{}^{(1,1)}t^{ad}_{kl}t^c_i\right)\\
&-\sum_{c,k,l}\langle l\,k||i\,c\rangle\left({}^{(1,1)}t^a_lt^c_k+{}^{(1,1)}t^c_kt^a_l+\frac{1}{2}{}^{(1,1)}t^{ac}_{lk}\right)-\sum_k d_{ki}\,{}^{(0,1)}t^a_k\\
&-\sum_{k,c}d_{kc}\,{}^{(0,1)}t^a_kt^c_i+\sum_c d_{ac}\,{}^{(0,1)}t^c_i-\sum_{c,k}d_{kc}\,{}^{(0,1)}t^c_it^a_k\\
&+\sum_{c,k}d_{kc}\,{}^{(0,1)}t^{ac}_{ik}-\sum_k h'_{ki}\,{}^{(1,0)}t^a_k-\sum_{k,c}h'_{kc}\,{}^{(1,0)}t^a_kt^c_i+\sum_c h'_{ac}\,{}^{(1,0)}t^c_i\\
&-\sum_{c,k}h'_{kc}\,{}^{(1,0)}t^c_it^a_k+\sum_{c,k}h'_{kc}\,{}^{(1,0)}t^{ac}_{ik}-\sum_{c,k}f_{kc}\left({}^{(0,1)}t^c_i\,{}^{(1,0)}t^a_k+{}^{(1,0)}t^c_i\,{}^{(0,1)}t^a_k\right)\\
&-\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^d_l\left({}^{(0,1)}t^c_i\,{}^{(1,0)}t^a_k+{}^{(1,0)}t^c_i\,{}^{(0,1)}t^a_k\right)+\sum_{c,k,d}\langle a\,k||c\,d\rangle\left({}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_k+{}^{(1,0)}t^c_i\,{}^{(0,1)}t^d_k\right)\\
&-\frac{1}{2}\sum_{k,l,c,d}\langle k\,l||c\,d\rangle\left({}^{(0,1)}t^c_i\,{}^{(1,0)}t^{ad}_{kl}+{}^{(1,0)}t^c_i\,{}^{(0,1)}t^{ad}_{kl}\right)-\sum_{k,l,c,d}\langle k\,l||c\,d\rangle t^a_k\left({}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_l+{}^{(1,0)}t^c_i\,{}^{(0,1)}t^d_l\right)\\
&-\sum_{c,k,l}\langle k\,l||i\,c\rangle\left({}^{(0,1)}t^a_k\,{}^{(1,0)}t^c_l+{}^{(1,0)}t^a_k\,{}^{(0,1)}t^c_l\right)-\frac{1}{2}\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\left({}^{(0,1)}t^a_k\,{}^{(1,0)}t^{cd}_{il}+{}^{(1,0)}t^a_k\,{}^{(0,1)}t^{cd}_{il}\right)\\
&-\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^c_i\left({}^{(0,1)}t^a_k\,{}^{(1,0)}t^d_l+{}^{(1,0)}t^a_k\,{}^{(0,1)}t^d_l\right)+\sum_{k,l,c,d}\langle k\,l||c\,d\rangle\left({}^{(0,1)}t^c_k\,{}^{(1,0)}t^{ad}_{il}+{}^{(1,0)}t^c_k\,{}^{(0,1)}t^{ad}_{il}\right)=0\,, \qquad \text{(A3)}
\end{aligned}
$$

and

$$
\begin{aligned}
&\langle\phi^{ab}_{ij}|\left(\{\bar{H}_NT^{(1,1)}\}_C+\{\bar{O}_1T^{(0,1)}\}_C+\{\bar{O}_2T^{(1,0)}\}_C+\{\bar{H}_NT^{(1,0)}T^{(0,1)}\}_C\right)|\phi_0\rangle\\
&=\sum_p(-1)^p P(ab)\sum_c f_{bc}\,{}^{(1,1)}t^{ac}_{ij}+\sum_p(-1)^p P(ab)\sum_{c,k,d}\langle k\,b||c\,d\rangle t^c_k\,{}^{(1,1)}t^{ad}_{ij}\\
&-\sum_p(-1)^p P(ab)\sum_{k,c}f_{kc}t^b_k\,{}^{(1,1)}t^{ac}_{ij}-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\,{}^{(1,1)}t^{ad}_{ij}\left(t^{cb}_{kl}+2t^c_kt^b_l\right)
\end{aligned}
$$

$$
\begin{aligned}
&-\sum_p(-1)^p P(ij)\sum_k f_{kj}\ {}^{(1,1)}t_{ik}^{ab} - \sum_p(-1)^p P(ij)\sum_{c,k} f_{kc}\ {}^{(1,1)}t_{ik}^{ab}t_j^c \\
&+\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\ l||c\ j\rangle t_k^c\ {}^{(1,1)}t_{il}^{ab} \\
&-\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{ckld}\langle k\ l||c\ d\rangle {}^{(1,1)}t_{il}^{ab}\left(t_{kj}^{cd}+2t_k^c t_j^d\right) \\
&+\sum_p(-1)^p P(ij)\sum_c\langle a\ b||i\ c\rangle {}^{(1,1)}t_j^c + \sum_p(-1)^p P(ij)\sum_{c,d}\langle a\ b||c\ d\rangle\ {}^{(1,1)}t_i^c t_j^d \\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k}\langle k\ a||c\ i\rangle\ {}^{(1,1)}t_j^c t_k^b - \sum_p(-1)^p P(ij)\sum_{c,k} f_{kc}\ {}^{(1,1)}t_j^c t_{ik}^{ab} \\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,d,k}\langle k\ b||c\ d\rangle\ {}^{(1,1)}t_j^c\left(t_k^a t_i^d + t_{ki}^{ad}\right) \\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\ l||c\ j\rangle\ {}^{(1,1)}t_i^c\left(t_{kl}^{ab}+t_k^a t_l^b\right) \\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_i^c\left(t_k^a t_{lj}^{db} - t_k^b t_{lj}^{da} + t_l^d t_{kj}^{ab}\right) \\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_i^c t_j^d\left(t_{kl}^{ab}+t_k^a t_l^b\right) \\
&-\sum_p(-1)^p P(ab)\sum_k\langle k\ a||j\ i\rangle\ {}^{(1,1)}t_k^b + \sum_p(-1)^p P(ab)\sum_{k,l}\langle k\ l||i\ j\rangle\ {}^{(1,1)}t_k^a t_l^b \\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k}\langle k\ a||c\ i\rangle\ {}^{(1,1)}t_k^b t_j^c - \sum_p(-1)^p P(ab)\sum_{k,c} f_{kc}\ {}^{(1,1)}t_k^b t_{ij}^{ac} \\
&+\sum_p(-1)^p P(ij|ab)\sum_{k,c,l}\langle l\ k||c\ j\rangle\ {}^{(1,1)}t_l^b\left(t_{ik}^{ca}+t_i^c t_k^a\right) \\
&-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{l,c,d}\langle l\ a||c\ d\rangle\ {}^{(1,1)}t_l^b\left(t_{ij}^{cd}+t_i^c t_j^d\right) \\
&-\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_k^b\left(t_j^c t_{il}^{ad} - t_i^c t_{jl}^{ad} + t_l^d t_{ij}^{ac}\right) \\
&+\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_l^b t_k^a\left(t_{ij}^{cd}+t_i^c t_j^d\right) \\
&+\frac{1}{2}\sum_{c,d}\langle a\ b||c\ d\rangle\ {}^{(1,1)}t_{ij}^{cd} - \frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,d,k}\langle a\ k||c\ d\rangle\ {}^{(1,1)}t_{ij}^{cd}t_k^b \\
&+\frac{1}{4}\sum_{c,d,k,l}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_{ij}^{cd}\left(t_{kl}^{ab}+t_k^a t_l^b\right) + \frac{1}{2}\sum_{k,l}\langle k\ l||i\ j\rangle\ {}^{(1,1)}t_{kl}^{ab} \\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\ l||i\ c\rangle\ {}^{(1,1)}t_{kl}^{ab}t_j^c + \frac{1}{4}\sum_{c,d,k,l}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_{kl}^{ab}\left(t_{ij}^{cd}+t_i^c t_j^d\right) \\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k}\langle a\ k||c\ i\rangle\ {}^{(1,1)}t_{jk}^{cb} - \sum_p(-1)^p P(ij|ab)\sum_{c,k,d}\langle a\ k||c\ d\rangle\ {}^{(1,1)}t_{ik}^{cb}t_j^d \\
&+\sum_p(-1)^p P(ij|ab)\sum_{k,l,c}\langle k\ l||i\ c\rangle\ {}^{(1,1)}t_{kj}^{ac}t_l^b \\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_{ik}^{ac}\left(t_{jl}^{db}+t_j^d t_l^b\right) \\
&+\sum_p(-1)^p P(ab)\sum_{c,k,d}\langle k\ b||c\ d\rangle\ {}^{(1,1)}t_k^c t_{ij}^{ad} - \sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\ l||c\ j\rangle\ {}^{(1,1)}t_k^c t_{il}^{ab} \\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_k^c t_j^d t_{il}^{ab} - \sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\ l||c\ d\rangle\ {}^{(1,1)}t_k^c t_l^b t_{ij}^{ad}
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\,{}^{(1,1)}t^{cd}_{kj}t^{ab}_{il}-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\,{}^{(1,1)}t^{cb}_{kl}t^{ad}_{ij}\\
&+\sum_p(-1)^p P(ab)\sum_c{}^{(0,1)}t^{ac}_{ij}\left(d_{bc}-\sum_k t^b_k d_{kc}\right)-\sum_p(-1)^p P(ij)\sum_k{}^{(0,1)}t^{ab}_{ik}\left(d_{kj}+\sum_c d_{kc}t^c_j\right)\\
&-\sum_p(-1)^p P(ij)\sum_{k,c}d_{kc}\,{}^{(0,1)}t^c_j t^{ab}_{ik}-\sum_p(-1)^p P(ab)\sum_{k,c}d_{kc}\,{}^{(0,1)}t^b_k t^{ac}_{ij}\\
&+\sum_p(-1)^p P(ab)\sum_c{}^{(1,0)}t^{ac}_{ij}\left(h'_{bc}-\sum_k t^b_k h'_{kc}\right)-\sum_p(-1)^p P(ij)\sum_k{}^{(1,0)}t^{ab}_{ik}\left(h'_{kj}+\sum_c h'_{kc}t^c_j\right)\\
&-\sum_p(-1)^p P(ij)\sum_{k,c}h'_{kc}\,{}^{(1,0)}t^c_j t^{ab}_{ik}-\sum_p(-1)^p P(ab)\sum_{k,c}h'_{kc}\,{}^{(1,0)}t^b_k t^{ac}_{ij}\\
&-\sum_p(-1)^p P(ab)\sum_{c,k}f_{kc}\left({}^{(1,0)}t^b_k\,{}^{(0,1)}t^{ac}_{ij}+{}^{(0,1)}t^b_k\,{}^{(1,0)}t^{ac}_{ij}\right)\\
&-\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^c_k\left({}^{(1,0)}t^b_l\,{}^{(0,1)}t^{ad}_{ij}+{}^{(0,1)}t^b_l\,{}^{(1,0)}t^{ad}_{ij}\right)\\
&+\sum_p(-1)^p P(ab)\sum_{c,k,d}\langle k\,b||c\,d\rangle\left({}^{(1,0)}t^c_k\,{}^{(0,1)}t^{ad}_{ij}+{}^{(0,1)}t^c_k\,{}^{(1,0)}t^{ad}_{ij}\right)\\
&-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\left({}^{(1,0)}t^{bc}_{lk}\,{}^{(0,1)}t^{ad}_{ij}+{}^{(0,1)}t^{bc}_{lk}\,{}^{(1,0)}t^{ad}_{ij}\right)\\
&-\sum_p(-1)^p P(ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^b_l\left({}^{(1,0)}t^c_k\,{}^{(0,1)}t^{ad}_{ij}+{}^{(0,1)}t^c_k\,{}^{(1,0)}t^{ad}_{ij}\right)\\
&-\sum_p(-1)^p P(ij)\sum_{c,k}f_{kc}\left({}^{(1,0)}t^c_j\,{}^{(0,1)}t^{ab}_{ik}+{}^{(0,1)}t^c_j\,{}^{(1,0)}t^{ab}_{ik}\right)\\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^c_k\left({}^{(1,0)}t^d_j\,{}^{(0,1)}t^{ab}_{il}+{}^{(0,1)}t^d_j\,{}^{(1,0)}t^{ab}_{il}\right)\\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\,l||c\,j\rangle\left({}^{(1,0)}t^c_k\,{}^{(0,1)}t^{ab}_{il}+{}^{(0,1)}t^c_k\,{}^{(1,0)}t^{ab}_{il}\right)\\
&-\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle\left({}^{(1,0)}t^{cd}_{kj}\,{}^{(0,1)}t^{ab}_{il}+{}^{(0,1)}t^{cd}_{kj}\,{}^{(1,0)}t^{ab}_{il}\right)\\
&-\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^d_j\left({}^{(1,0)}t^c_k\,{}^{(0,1)}t^{ab}_{il}+{}^{(0,1)}t^c_k\,{}^{(1,0)}t^{ab}_{il}\right)\\
&+\sum_p(-1)^p P(ij)\sum_{c,d}\langle a\,b||c\,d\rangle\,{}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_j-\sum_p(-1)^p P(ij|ab)\sum_{c,k,d}\langle a\,k||c\,d\rangle t^b_k\,{}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_j\\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^{ab}_{kl}\,{}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_j\\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^a_k\,t^b_l\,{}^{(0,1)}t^c_i\,{}^{(1,0)}t^d_j\\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k}\langle k\,a||c\,i\rangle\left({}^{(1,0)}t^b_k\,{}^{(0,1)}t^c_j+{}^{(0,1)}t^b_k\,{}^{(1,0)}t^c_j\right)\\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k,d}\langle k\,b||c\,d\rangle t^d_j\left({}^{(1,0)}t^a_k\,{}^{(0,1)}t^c_i+{}^{(0,1)}t^a_k\,{}^{(1,0)}t^c_i\right)\\
&+\sum_p(-1)^p P(ij|ab)\sum_{c,k,l}\langle k\,l||c\,j\rangle t^b_l\left({}^{(1,0)}t^a_k\,{}^{(0,1)}t^c_i+{}^{(0,1)}t^a_k\,{}^{(1,0)}t^c_i\right)\\
&+\sum_p(-1)^p P(ij|ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^d_j t^b_l\left({}^{(1,0)}t^a_k\,{}^{(0,1)}t^c_i+{}^{(0,1)}t^a_k\,{}^{(1,0)}t^c_i\right)\\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^{ad}_{il}\left({}^{(1,0)}t^b_k\,{}^{(0,1)}t^c_j+{}^{(0,1)}t^b_k\,{}^{(1,0)}t^c_j\right)
\end{aligned}
$$

$$
\begin{aligned}
&-\sum_p(-1)^p P(ij|ab)\sum_{c,d,k}\langle k\,b||c\,d\rangle\left({}^{(1,0)}t^{ad}_{ki}\,{}^{(0,1)}t^{c}_{j}+{}^{(0,1)}t^{ad}_{ki}\,{}^{(1,0)}t^{c}_{j}\right)\\
&-\sum_p(-1)^p P(ij|ab)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^{b}_{k}\left({}^{(1,0)}t^{ad}_{il}\,{}^{(0,1)}t^{c}_{j}+{}^{(0,1)}t^{ad}_{il}\,{}^{(1,0)}t^{c}_{j}\right)\\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l}\langle k\,l||c\,j\rangle\left({}^{(1,0)}t^{ab}_{kl}\,{}^{(0,1)}t^{c}_{i}+{}^{(0,1)}t^{ab}_{kl}\,{}^{(1,0)}t^{c}_{i}\right)\\
&+\frac{1}{2}\sum_p(-1)^p P(ij)\sum_{c,k,l,d}\langle k\,l||c\,d\rangle t^{d}_{j}\left({}^{(1,0)}t^{ab}_{kl}\,{}^{(0,1)}t^{c}_{i}+{}^{(0,1)}t^{ab}_{kl}\,{}^{(1,0)}t^{c}_{i}\right)+\sum_p(-1)^p P(ab)\sum_{k,l}\langle k\,l||i\,j\rangle\,{}^{(1,0)}t^{b}_{l}\,{}^{(0,1)}t^{a}_{k}\\
&+\sum_p(-1)^p P(ij|ab)\sum_{k,l,c}\langle k\,l||i\,c\rangle t^{c}_{j}\,{}^{(1,0)}t^{b}_{l}\,{}^{(0,1)}t^{a}_{k}\\
&+\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{k,l,c,d}\langle k\,l||c\,d\rangle t^{cd}_{ij}\,{}^{(1,0)}t^{b}_{l}\,{}^{(0,1)}t^{a}_{k}\\
&+\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{k,c,l,d}\langle k\,l||c\,d\rangle t^{c}_{i}t^{d}_{j}\,{}^{(1,0)}t^{b}_{l}\,{}^{(0,1)}t^{a}_{k}\\
&+\sum_p(-1)^p P(ij|ab)\sum_{k,c,l}\langle k\,l||c\,j\rangle\left({}^{(1,0)}t^{cb}_{il}\,{}^{(0,1)}t^{a}_{k}+{}^{(0,1)}t^{cb}_{il}\,{}^{(1,0)}t^{a}_{k}\right)\\
&-\sum_p(-1)^p P(ij|ab)\sum_{k,c,l,d}\langle k\,l||c\,d\rangle t^{c}_{j}\left({}^{(1,0)}t^{ad}_{il}\,{}^{(0,1)}t^{b}_{k}+{}^{(0,1)}t^{ad}_{il}\,{}^{(1,0)}t^{b}_{k}\right)\\
&-\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{k,c,d}\langle k\,b||c\,d\rangle\left({}^{(1,0)}t^{cd}_{ij}\,{}^{(0,1)}t^{a}_{k}+{}^{(0,1)}t^{cd}_{ij}\,{}^{(1,0)}t^{a}_{k}\right)\\
&+\frac{1}{2}\sum_p(-1)^p P(ab)\sum_{k,c,l,d}\langle k\,l||c\,d\rangle t^{b}_{l}\left({}^{(1,0)}t^{cd}_{ij}\,{}^{(0,1)}t^{a}_{k}+{}^{(0,1)}t^{cd}_{ij}\,{}^{(1,0)}t^{a}_{k}\right)\\
&+\frac{1}{4}\sum_{c,d,k,l}\langle k\,l||c\,d\rangle\left({}^{(1,0)}t^{ab}_{kl}\,{}^{(0,1)}t^{cd}_{ij}+{}^{(0,1)}t^{ab}_{kl}\,{}^{(1,0)}t^{cd}_{ij}\right)\\
&+\sum_p(-1)^p P(ij|ab)\sum_{c,d,k,l}\langle k\,l||c\,d\rangle\,{}^{(1,0)}t^{bd}_{jl}\,{}^{(0,1)}t^{ac}_{ik}\\
&-\sum_p(-1)^p P(ij)\sum_{c,d,k,l}\langle k\,l||c\,d\rangle t^{ab}_{il}\left({}^{(1,0)}t^{c}_{k}\,{}^{(0,1)}t^{d}_{j}+{}^{(0,1)}t^{c}_{k}\,{}^{(1,0)}t^{d}_{j}\right)\\
&-\sum_p(-1)^p P(ab)\sum_{c,d,k,l}\langle k\,l||c\,d\rangle t^{ad}_{ij}\left({}^{(1,0)}t^{c}_{k}\,{}^{(0,1)}t^{b}_{l}+{}^{(0,1)}t^{c}_{k}\,{}^{(1,0)}t^{b}_{l}\right)=0\,. \qquad \text{(A4)}
\end{aligned}
$$

The permutation operators, $\sum_p(-1)^p P(ij)$, $\sum_p(-1)^p P(ab)$ and $\sum_p(-1)^p P(ij|ab)$, used in the equations above, have been introduced to make the algebraic expressions fully antisymmetric with respect to interchange of hole (i, j) and particle (a, b) indices [5,22]. The symbol $P(ab)$ preceding an algebraic expression means that in addition to the identity permutation (parity factor $+1$), there is a single permutation (parity factor -1) of a with b. However, the symbol $P(ij|ab)$ means that i can be permuted with j and not a and b, and similarly a and b can be permuted among themselves and not with i and j.

Finally, we get the algebraic expression for $E^{(1,1)}$ as defined in Eq. (43) to be

$$
\begin{aligned}
E^{(1,1)}=&\sum_{k,c}f_{kc}\,{}^{(1,1)}t^{c}_{k}+\sum_{k,c,l,d}\langle k\,l||c\,d\rangle\left({}^{(1,1)}t^{c}_{k}\,t^{d}_{l}+\frac{1}{4}\,{}^{(1,1)}t^{cd}_{kl}\right)+\sum_{c,k}h'_{kc}\,{}^{(1,0)}t^{c}_{k}\\
&+\sum_{c,k}d_{kc}\,{}^{(0,1)}t^{c}_{k}+\sum_{k,l,c,d}\langle k\,l||c\,d\rangle\,{}^{(1,0)}t^{c}_{k}\,{}^{(0,1)}t^{d}_{l}\,. \qquad \text{(A5)}
\end{aligned}
$$

In the equations above, f_{pq} represents the one-electron matrix elements, and $\langle pq||rs\rangle=\langle pq|1/r_{12}|rs\rangle-\langle pq|1/r_{12}|sr\rangle$ denotes the antisymmetrized Coulomb repulsion matrix elements of the unperturbed Hamiltonian H.

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