

On the calculation of second order properties: An equation of motion approach

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Abstract. In the light of the equation of motion method a general expression for polarisability calculation has been derived. From this general expression, different approximation methods can be deduced for different choices of ground state and excitation manifold. Among these the coupled Hartree-Fock theory is the most extensively used one for polarisability calculations. It has also been shown that this theory has a simple relationship with random phase approximation.

Keywords. Second order properties; equation of motion; polarisability; Hartree-Fock theory; random phase approximation.

1. Introduction

Accurate calculations of transition energies for multi-electronic systems have received considerable attention and remain the main testing ground for the choice of basis and electron-correlation theories. The other important property which is equally sensitive to these factors is the polarisability of a molecular system, since in its calculation both the ground state and the excited states of the system are involved. Systematic studies to this end have not received much importance till now.

The coupled Hartree-Fock theories (CHFT) either time-independent (Langhoff *et al* 1966) or time-dependent (McLachlan 1964; McLachlan and Ball 1964) versions and their variants (Langhoff *et al* 1972; McWeeny 1962; Dierksen and McWeeny 1966; Dodds *et al* 1977) have been the most extensively used ones for the polarisability calculations. Caves and Karplus (1969) showed, using perturbative arguments, that the CHFT include some electron correlation and in fact, they sum up some hole-particle ladder diagrams to all orders. Mukherjee *et al* (1979) pointed out that coupled cluster-based linear response theory can be utilised to calculate the dynamic polarisability. Monkhorst (1977) also used correlated wavefunction (using coupled cluster-formalism) for deriving the polarisability expression.

The EOM methods (Dunning and McKoy 1967; Shibuya *et al* 1973; McCardy *et al* 1977) are highly successful in generating hierarchy of equations for difference-energy calculations. In this paper we use the spirit of EOM methods to derive a general expression for polarisability (both static and dynamic). We shall give the outline of a few approximation methods, besides CHFT, which may be used to calculate molecular polarisabilities. These methods take into account the correlation effect explicitly and

are expected to give better results. We shall also show the relationship between CHFT and random phase approximation (RPA) in a very simple and straight-forward manner.

2. Theory

We first consider the ordinary perturbation equation:

$$(H_0 + V)|\psi\rangle = E|\psi\rangle. \quad (1)$$

We now write the Rayleigh-Schrödinger perturbation equations as

$$H_0|O\rangle = E_0|O\rangle. \quad (2)$$

$$(H_0 - E_0)|\psi^{(1)}\rangle + (V - E^{(1)})|O\rangle = 0. \quad (3)$$

The second order energy is given by

$$E^{(2)} = \langle O|V|\psi^{(1)}\rangle, \quad (4)$$

$$\text{with } \langle \psi^{(1)}|O\rangle = 0. \quad (5)$$

$|\psi^{(1)}\rangle$ is generated by operating S^\dagger on $|O\rangle$,

$$|\psi^{(1)}\rangle = S^\dagger|O\rangle. \quad (6)$$

Equation (5) then implies

$$\langle O|S|O\rangle = 0.$$

Now, if we choose S in such a way that

$$S|O\rangle = 0, \quad (7)$$

the above condition is readily satisfied.

Equation (7) is then the well-known "Killer condition" and S^\dagger is the excitation operator. Equation (3) can now be written as

$$(H_0 - E_0)S^\dagger|O\rangle + (V - E^{(1)})|O\rangle = 0,$$

which, with the help of (2), becomes

$$[H_0, S^\dagger]|O\rangle + (V - E^{(1)})|O\rangle = 0. \quad (8)$$

The second-order energy, $E^{(2)}$, may be written in a commutator form, using (7),

$$E^{(2)} = \langle O|[V, S^\dagger]|O\rangle. \quad (9a)$$

The commutator form of (9a) has got a definite practical advantage, since for approximate $|O\rangle$, a better accuracy of the average value is generally expected with a reduced particle rank operator (McCurdy *et al* 1977). Thus the polarisability, α , is given by

$$\begin{aligned} \alpha &= 2E^{(2)}, \\ &= 2\langle O|[V, S^\dagger]|O\rangle. \end{aligned} \quad (9b)$$

Now, we have to approximate S^\dagger and $|O\rangle$; depending on different choices of S^\dagger and $|O\rangle$ we have different sets of equations.

In the following two sections we shall develop different approximate theories for static and dynamic polarisabilities.

3. Static polarisability

In developing a theory for calculating static polarisability we assume H_0 to be the molecular hamiltonian in occupation number representation with HF state, $|\Phi_{\text{HF}}\rangle$, as vacuum:

$$H_0 = E_{\text{HF}} + \sum_i \varepsilon_i N[a_i^\dagger a_i] + \frac{1}{2} \sum_{ijkl} \langle ij|v|kl\rangle N[a_i^\dagger a_j^\dagger a_l a_k].$$

The perturbation V is any one-electron operator of the form

$$V = \sum_{ij} \langle i|v|j\rangle a_i^\dagger a_j.$$

Now, depending on different choices of S^\dagger and $|O\rangle$ different sets of equations can be formulated as follows:

3.1 Coupled Hartree-Fock theory

We shall first of all proceed to develop CHF theory from (8). Using the Killer condition (7) we can rearrange (8) as

$$[S, [H_0, S^\dagger]]|O\rangle + [S, V]|O\rangle = 0. \quad (10)$$

We then write this equation in an "expectation value" form,

$$\langle O|[S, [H_0, S^\dagger]]|O\rangle + \langle O|[S, V]|O\rangle = 0. \quad (11)$$

It may be noted that (11) is unsymmetrical with respect to S and S^\dagger which is clearly unsuitable for variation. Following Rowe (1968), we now symmetrise (11) by adding to itself its hermitian conjugate. The final form of the equation is

$$\langle O|[S, H_0, S^\dagger]|O\rangle + \frac{1}{2}\langle O|[V, S^\dagger]|O\rangle + \frac{1}{2}\langle O|[S, V]|O\rangle = 0 \quad (12)$$

where the triple commutator, $[S, H_0, S^\dagger]$, is given by

$$[S, H_0, S^\dagger] = \frac{1}{2}[S, [H_0, S^\dagger]] + \frac{1}{2}[[S, H_0], S^\dagger].$$

We now approximate $|O\rangle$ as $|\Phi_{\text{HF}}\rangle$ and S^\dagger as a linear combination of $1h - 1p$ excitation and de-excitation operators:

$$S^\dagger = \sum_{am} \langle m|g|\alpha\rangle a_m^\dagger a_\alpha - \sum_{am} \langle \alpha|h|m\rangle a_\alpha^\dagger a_m,$$

where the roman alphabets indicate particle orbitals and the Greek letters hole orbitals.

These are precisely the approximations used in deriving RPA theory and we can proceed in the same way to arrive at the equations:

$$\sum_{n\beta} (A_{m\alpha, n\beta} \langle n|g|\beta\rangle + B_{m\alpha, n\beta} \langle \beta|h|n\rangle) + \frac{1}{2}\langle m|V|\alpha\rangle = 0, \quad (13a)$$

and

$$\sum_{n\beta} (A_{m\alpha, n\beta}^* \langle \beta|h|n\rangle + B_{m\alpha, n\beta}^* \langle n|g|\beta\rangle) + \frac{1}{2}\langle \alpha|V|m\rangle = 0, \quad (13b)$$

where,

$$A_{m\alpha, n\beta} = (\varepsilon_m - \varepsilon_\alpha)\delta_{mn}\delta_{\alpha\beta} + 2\langle m\beta|v|\alpha n\rangle - \langle m\beta|v|n\alpha\rangle,$$

and

$$B_{m\alpha, n\beta} = 2\langle mn|v|\alpha\beta\rangle - \langle mn|v|\beta\alpha\rangle.$$

Equation (13b) is just the complex conjugate of (13a) with only the roles of g and h matrices interchanged; whence, it follows

$$\langle \beta | h | n \rangle = \langle n | g | \beta \rangle^* \quad (14)$$

Substituting (14) in (13a) we get,

$$\sum_{n\beta} (A_{m\alpha, n\beta} g_{n\beta} + B_{m\alpha, n\beta} g_{n\beta}^*) + \frac{1}{2} V_{m\alpha} = 0, \quad (15a)$$

where, $g_{m\alpha} = \langle m | g | \alpha \rangle$ and $V_{m\alpha} = \langle m | V | \alpha \rangle$.

Substituting the full expressions for A , B matrix-elements, we have

$$\begin{aligned} (\varepsilon_m - \varepsilon_\alpha) g_{m\alpha} + \sum_{n\beta} \{ [2 \langle m\beta | v | \alpha n \rangle - \langle m\beta | v | n\alpha \rangle] g_{n\beta} \\ + [2 \langle mn | v | \alpha\beta \rangle - \langle mn | v | \beta\alpha \rangle] g_{n\beta}^* \} + \frac{1}{2} V_{m\alpha} = 0. \end{aligned} \quad (15b)$$

Equation (15b) may be compared with CHFT-equation derived by Langhoff *et al* (1966). The factor 1/2 appearing in the last term of the equation is due to symmetrisation. However, $E^{(2)}$ can now be calculated using (9) and is identical with the CHFT.

A drawback of CHFT is that the de-excitation part gets undue emphasis, being equal in weightage to the excitation part itself [$h_{am} = g_{m\alpha}^*$] and we may get an over-correlated wavefunction. This difficulty may be overcome by approximating $|O\rangle$ a little differently as

$$\begin{aligned} |O\rangle &= |\Phi_{\text{HF}}\rangle + |\Phi_{\text{doubly-excited}}\rangle, \\ &= |\Phi_{\text{HF}}\rangle + |\Phi_{\alpha\beta}^{mn}\rangle, \\ &= |\Phi_{\text{HF}}\rangle + \frac{1}{2} \sum_{\substack{m\alpha \\ n\beta}} C_{\alpha\beta}^{mn} a_m^\dagger a_n^\dagger a_\beta a_\alpha |\Phi_{\text{HF}}\rangle, \\ &= \left(1 + \frac{1}{2} \sum_{\substack{m\alpha \\ n\beta}} C_{\alpha\beta}^{mn} a_m^\dagger a_n^\dagger a_\beta a_\alpha \right) |\Phi_{\text{HF}}\rangle, \end{aligned}$$

and evaluating h per force from (7) as follows:

$$S|O\rangle = 0,$$

$$\text{or, } \sum_{m\alpha} (g^* C - h^*)_{m\alpha} a_m^\dagger a_\alpha |\Phi_{\text{HF}}\rangle = 0.$$

Projecting this equation by $\langle \Phi_\alpha^m |$, we have

$$\langle \Phi_\alpha^m | \sum_{m\alpha} (g^* C - h^*)_{m\alpha} a_m^\dagger a_\alpha |\Phi_{\text{HF}}\rangle = 0,$$

from which it follows

$$h = C^\dagger g.$$

The matrix-elements of C^\dagger can be calculated variationally or by perturbative methods or by linearised coupled cluster formalism. Now, substituting the value of h in (13a) we get an equation similar in form to (15a), involving g only, and subsequently we can evaluate $E^{(2)}$ as before.

3.2 Tamm–Dancoff like approximation using $1h - 1p$ and $2h - 2p$ excitation

In this case, instead of choosing S^\dagger as $1h - 1p$ excitation and de-excitation form, we approximate it as

$$S^\dagger = \sum_{m\alpha} \langle m|s_1|\alpha\rangle a_m^\dagger a_\alpha + \frac{1}{2} \sum_{m\alpha, n\beta} \langle mn|s_2|\alpha\beta\rangle a_m^\dagger a_n^\dagger a_\beta a_\alpha \quad (16)$$

while $|O\rangle$ remains as $|\Phi_{HF}\rangle$.

We may straightaway start with (8) and project it with $1h - 1p$ and $2h - 2p$ excited states $|\Phi_\alpha^m\rangle$ and $|\Phi_{\alpha\beta}^{mn}\rangle$, obtained from $|\Phi_{HF}\rangle$ the ground state, to get the s_1 - and s_2 -determining equations,

$$\sum_{n\beta} A_{m\alpha; n\beta} \langle n|s_1|\beta\rangle + \sum_{p\gamma, n\beta} C_{m\alpha; p\gamma, n\beta} \langle pn|s_2|\gamma\beta\rangle + \langle m|V|\alpha\rangle = 0, \quad (17)$$

and

$$\sum_{p\gamma} D_{m\alpha, n\beta; p\gamma} \langle p|s_1|\gamma\rangle + \sum_{p\gamma, q\delta} E_{m\alpha, n\beta; p\gamma, q\delta} \langle pq|s_2|\gamma\delta\rangle = 0. \quad (18)$$

The matrices A, C, D, E can be generated easily by diagrammatic techniques. The final expressions for the matrices are given in Appendix 1.

From (17) and (18) s_1 and s_2 vectors can easily be calculated and thus the second-order energy, $E^{(2)}$, may be evaluated using (9). It may be noted at this point, that in computing $E^{(2)}$ by (9) we require only the completely contracted terms with V and S^\dagger . Since V is a one-body operator, we can have only terms involving V and s_1 . The two-body term, which takes into account the correlation effect, is effective only indirectly and we may take advantage of this situation by simply eliminating s_2 from (17) and (18) as

$$s_2 = -E^{-1}Ds_1,$$

and s_1 determining equation now becomes

$$(A - CE^{-1}D)s_1 + V = 0. \quad (19)$$

Here the effect of s_2 has been actually “folded in” and hence we may interpret (19) as an “effective hamiltonian” formalism.

3.3 Use of coupled cluster formalism

In §§ 3.1 and 3.2 we have some inconsistency in our approximation. We have assumed H_0 to be the exact molecular hamiltonian of the system, while $|O\rangle$ is approximated as $|\Phi_{HF}\rangle$. In order to obviate this difficulty we may start from a more accurate description in which the effect of correlation in $|O\rangle$ is taken into consideration explicitly.

The couple cluster formalism is the one in which the correlation is incorporated in an elegant fashion. We can write following (Cizek 1966),

$$|O\rangle = e^T|\Phi_{HF}\rangle,$$

where T in general is a sum of $nh - np$ excitation operators.

$$T = \sum_n T_n.$$

where T_n is the $nh - np$ excitation operator,

$$T_n = \frac{1}{n!} \sum \langle pqr \dots | t_n | \alpha\beta\gamma \dots \rangle a_p^\dagger a_q^\dagger a_r^\dagger \dots a_\gamma a_\beta a_\alpha.$$

Equation (8) under this condition becomes

$$[H_0, S^\dagger] e^T |\Phi_{\text{HF}}\rangle + (V - E^{(1)}) e^T |\Phi_{\text{HF}}\rangle = 0. \quad (20)$$

S^\dagger and T are both hole-particle excitation operators and so they commute; (20) then takes the form

$$[\bar{H}_0, S^\dagger] |\Phi_{\text{HF}}\rangle + (\bar{V} - E^{(1)}) |\Phi_{\text{HF}}\rangle = 0.$$

where $\bar{H}_0 = e^{-T} H_0 e^T$ and $\bar{V} = e^{-T} V e^T$. (21)

Now we can proceed in the same way as in §3.2 to get,

$$\left. \begin{aligned} \bar{A}s_1 + \bar{c}s_2 + \bar{V}_1 &= 0 \\ \bar{D}s_1 + \bar{E}s_2 + \bar{V}_2 &= 0 \end{aligned} \right\} \quad (22)$$

where $\bar{A}, \bar{C}, \bar{D}, \bar{E}$ have the same expressions as in §3.2; only the integrals appearing in A, C, D, E are replaced by transformed ones according to (21). \bar{V}_1 and \bar{V}_2 are the one-body and two-body parts of transformed V operator. For most molecular systems it is well-known that the two-body term in T makes the largest and significant contribution and so we may approximate T as

$$T \cong T_2.$$

In order to carry out the calculation we have to solve t_2 by following the formalism of Cizek (1966). Once the t_2 's are known we can evaluate s_1 and s_2 by (22).

To determine the second-order energy, $E^{(2)}$, in this formalism it requires some special considerations:

(i) Since we have defined $|O\rangle$ as

$$|O\rangle = e^T |\Phi_{\text{HF}}\rangle.$$

$|O\rangle$ is no longer normalised.

(ii) We may write the unperturbed Schrödinger equation as

$$\begin{aligned} H_0 e^T |\Phi_{\text{HF}}\rangle &= E_0 e^T |\Phi_{\text{HF}}\rangle \\ \bar{H}_0 |\Phi_{\text{HF}}\rangle &= E_0 |\Phi_{\text{HF}}\rangle \end{aligned}$$

H_0 has lost its hermiticity in \bar{H}_0 ($\langle \Phi_{\text{HF}} | \bar{H}_0 \neq E_0 \langle \Phi_{\text{HF}} |$).

We may have two different choices for determining $E^{(2)}$. We start by writing the $E^{(2)}$ determining equation,

$$(H_0 - E_0) |\Psi^{(2)}\rangle + (V - E^{(1)}) |\Psi^{(1)}\rangle - E^{(2)} |O\rangle = 0. \quad (23)$$

Choice A: We now proceed to evaluate $E^{(2)}$ by projecting (23) by $\langle O|$; in that case

$$\langle O | (H_0 - E_0) |\Psi^{(2)}\rangle + \langle O | (V - E^{(1)}) |\Psi^{(1)}\rangle - E^{(2)} \langle O | O \rangle = 0,$$

so that, $E^{(2)} = \langle O | V | \Psi^{(1)} \rangle / \langle O | O \rangle$.

This equation may be written as

$$\begin{aligned} E^{(2)} &= \frac{\langle O|[V, S_1^\dagger]|O\rangle}{\langle O|O\rangle} \quad \text{using Killer condition.} \\ &= \frac{\langle \Phi_{\text{HF}}|e^{T^\dagger}[V, S_1^\dagger]e^T|\Phi_{\text{HF}}\rangle}{\langle \Phi_{\text{HF}}|e^{T^\dagger}e^T|\Phi_{\text{HF}}\rangle}, \\ &= \langle \Phi_{\text{HF}}|e^{T^\dagger}[V, S_1^\dagger]e^T|\Phi_{\text{HF}}\rangle_{\text{linked}}. \end{aligned}$$

Choice B: We may write $|\Psi^{(2)}\rangle$ as

$$|\Psi^{(2)}\rangle = S_2^\dagger|O\rangle,$$

where S_2^\dagger is some excitation operator (since $\langle \Psi^{(2)}|O\rangle = 0$).

In that case, we can write (23) as

$$[H_0, S_2^\dagger]|O\rangle + (V - E^{(1)})S_1^\dagger|O\rangle - E^{(2)}|O\rangle = 0.$$

This equation may be rearranged to give

$$[\bar{H}_0, S_2^\dagger]|\Phi_{\text{HF}}\rangle + (\bar{V} - E^{(1)})S_1^\dagger|\Phi_{\text{HF}}\rangle - E^{(2)}|\Phi_{\text{HF}}\rangle = 0.$$

Projecting with $\langle \Phi_{\text{HF}}|$, we get

$$E^{(2)} = \langle \Phi_{\text{HF}}|[\bar{H}_0, S_2^\dagger]|\Phi_{\text{HF}}\rangle + \langle \Phi_{\text{HF}}|[\bar{V}, S_1^\dagger]|\Phi_{\text{HF}}\rangle,$$

using (7) for S_1^\dagger .

This expression of $E^{(2)}$ is similar to that given by Mukherjee *et al* (1979), and also by Monkhorst (1977). It may be noted that the first term is non-vanishing because \bar{H}_0 is not hermitian. So in order to determine $E^{(2)}$, we have to evaluate S_2 and that can be done exactly in the same fashion as for S_1 .

Each choice has its own advantage. For *Choice A*, we need not have to generate $|\Psi^{(2)}\rangle$ to evaluate $E^{(2)}$ and the expression is simple if we retain the terms linear in T , but the expression becomes unwieldy if we go beyond the linear terms.

For *Choice B*, the expression remains simple even for nonlinear T . Moreover, for the determination of S_2^\dagger if we truncate the excitation operator S_2^\dagger after $2h - 2p$ excitations we have the same sets of $\bar{A}, \bar{C}, \bar{D}, \bar{E}$ as for S_1^\dagger . Only the \bar{V} terms in (22) get modified.

4. Dynamic polarisability

Generally, to derive the expression for dynamic polarisability, one starts with a time-dependent equation and treat the interaction hamiltonian explicitly time-dependent. One then encounters the ‘‘secular’’ terms in perturbation expansion which are difficult to eliminate. We shall show presently that we may obviate this by assuming the molecular system to be embedded in a photon field with which it is interacting. So we may write

$$H_0 = H_M^0 + H_{\text{ph}},$$

where, H_M^0 is the molecular hamiltonian, H_{ph} is the photon hamiltonian.

$$H_{\text{ph}} = \hbar\omega C^\dagger C,$$

where C^\dagger, C are the photon creation and annihilation operators.

The perturbation part V is given by (Loudon 1978)

$$V = \left[ie \sum_{i,j} \left(\frac{\hbar\omega}{2\varepsilon_0 V} \right)^{1/2} \varepsilon_{ij} \langle i|V|j\rangle a_i^\dagger a_j \right] (C - C^\dagger) \\ \equiv V_{sp} (C - C^\dagger)$$

where V_{sp} is the spatial part of the perturbation.

The unperturbed wave function should now have two parts: (a) $|\Psi_0\rangle$ describing unperturbed molecular system; (b) $|\chi_{ph}\rangle$ for the description of photon field (with n photons). Under this condition (8) becomes

$$[H_0, S^\dagger] |\Psi_0 \chi_{ph}\rangle + [V_{sp} (C - C^\dagger) - E^{(1)}] |\Psi_0 \chi_{ph}\rangle = 0. \quad (24)$$

Now we choose S^\dagger as

$$S^\dagger = S_{sp}^\dagger (C - C^\dagger),$$

so that (24) becomes

$$[H_M^0, S_{sp}^\dagger] (C - C^\dagger) |\Psi_0 \chi_{ph}\rangle + S_{sp}^\dagger [H_{ph}, (C - C^\dagger)] |\Psi_0 \chi_{ph}\rangle \\ + [V_{sp} (C - C^\dagger) - E^{(1)}] |\Psi_0 \chi_{ph}\rangle = 0,$$

which on simplification gives

$$[H_M^0, S_{sp}^\dagger] (C - C^\dagger) |\Psi_0 \chi_{ph}\rangle - S_{sp}^\dagger \hbar\omega (C + C^\dagger) |\Psi_0 \chi_{ph}\rangle \\ + [V_{sp} (C - C^\dagger) - E^{(1)}] |\Psi_0 \chi_{ph}\rangle = 0. \quad (25)$$

Projecting the equation by $\langle \chi_{ph}^\pm |$ states (where \pm indicate photon states with $n \pm 1$ photons), we have two equations

$$[H_M^0, S_{sp}^\dagger] |\Psi_0\rangle - \hbar\omega S_{sp}^\dagger |\Psi_0\rangle + V_{sp} |\Psi_0\rangle = 0, \quad (26a)$$

$$\text{and} \quad [H_M^0, S_{sp}^\dagger] |\Psi_0\rangle + \hbar\omega S_{sp}^\dagger |\Psi_0\rangle + V_{sp} |\Psi_0\rangle = 0. \quad (26b)$$

Equations (26) are similar to that for the static polarisability. The only difference is the appearance of the term involving $\pm \hbar\omega$ in (26).

Here again, depending on different sets of choice $|\Psi_0\rangle$ and S_{sp}^\dagger we have different expressions for the $S_{sp}^\dagger(\pm\omega)$ determining equations. Once the $S_{sp}^\dagger(\pm\omega)$ are known the dynamic polarisability of the molecular system can easily be calculated by (9) neglecting the photon self-energy term,

$$E^{(2)} = \langle \Psi_0 | [V_{sp}, S_{sp}^\dagger] | \Psi_0 \rangle, \\ = \langle \Psi_0 | [V_{sp}, S_{sp}^\dagger(+\omega)] | \Psi_0 \rangle \\ + \langle \Psi_0 | [V_{sp}, S_{sp}^\dagger(-\omega)] | \Psi_0 \rangle. \quad (27)$$

In a forthcoming publication we shall report the calculation of dipole polarisability of some simple molecular system using extended CNDO basis and CHF theory. We shall also try to make a comparative study of the different methods proposed here.

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Appendix 1

$$A_{m\alpha; n\beta} = \langle m|f|n\rangle\delta_{\alpha\beta} - \langle\beta|f|\alpha\rangle\delta_{mn} + 2\langle m\beta|v|\alpha n\rangle - \langle m\beta|v|n\alpha\rangle$$

$$C_{m\alpha; p\gamma; n\beta} = [2\langle m\beta|v|pn\rangle - \langle m\beta|v|np\rangle]\delta_{\alpha\gamma} \\ - [2\langle\gamma\beta|v|\alpha n\rangle - \langle\gamma\beta|v|n\alpha\rangle]\delta_{mp}$$

$$D_{m\alpha; n\beta; p\gamma} = \langle mn|v|\alpha p\rangle\delta_{\gamma\beta} - \langle m\gamma|v|\alpha\beta\rangle\delta_{pn}$$

$$E_{m\alpha; n\beta; p\gamma; q\delta} = \langle m|f|p\rangle\delta_{nq}\delta_{\alpha\gamma}\delta_{\beta\delta} - \langle\gamma|f|\alpha\rangle\delta_{pm}\delta_{qn}\delta_{\beta\delta} \\ + \frac{1}{2}\langle mn|v|pq\rangle\delta_{\alpha\gamma}\delta_{\beta\delta} + \frac{1}{2}\langle\gamma\delta|v|\alpha\beta\rangle\delta_{mp}\delta_{nq} \\ + [2\langle n\gamma|v|\beta p\rangle - \langle n\gamma|v|p\beta\rangle]\delta_{mq}\delta_{\alpha\delta} \\ - \langle n\gamma|v|\beta q\rangle\delta_{mp}\delta_{\alpha\delta} - \langle m\gamma|v|q\beta\rangle\delta_{pn}\delta_{\alpha\delta}$$

where, f refers to the Fock operator.

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