Higher-Order Calculations of Atomic Polarizabilities

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June 20, 2001

Abstract

A scheme for direct evaluating atomic polarizabilities of atoms with one valence electron starting from all-order SD wave functions is proposed.

1 Introduction

In this note, we consider a direct approach to evaluating the polarizability of an atom. A similar approach could be used to determine PNC amplitudes. We consider a atom in a state Ψ_v. We assume, for the present, that Ψ_v is an exact wave function; later we approximate it by an SD wave function. We introduce a field $\mathcal{E}$ directed along the z-axis. The interaction of this field with the atom is described by the Hamiltonian

$$H_{\mathrm{ext}} = -e\mathcal{E}\sum_{i=1}^{N} z_i = -e\mathcal{E}\sum_{ij} z_{ij} a_i^\dagger a_j, \tag{1}$$

where the two forms are appropriate to first- and second-quantization, respectively. The exact ground-state wave function Ψ_v satisfies the Schrödinger equation

$$(H_0 + V)\Psi_v = E_v \Psi_v. \tag{2}$$

The first-order energy shift caused by the perturbation H_{ext} is

$$E_v^{(1)} = \langle \Psi_v | H_{\mathrm{ext}} | \Psi_v \rangle = 0. \tag{3}$$

The fact that the first-order energy vanishes is a consequence of the odd parity of z_i. The first-order correction to the wave function satisfies the inhomogeneous equation

$$(H_0 + V - E_v)\Psi_v^{(1)} = -H_{\mathrm{ext}}\Psi_v, \tag{4}$$

and the second-order energy is given in terms of the first-order wave function by

$$
\begin{aligned}
E_v^{(2)} &= \langle \Psi_v | H_{\rm ext} | \Psi_v^{(1)} \rangle \\
&= \sum_n \frac{\langle \Psi_v | H_{\rm ext} | \Psi_n \rangle \langle \Psi_n | H_{\rm ext} | \Psi_v \rangle}{E_v - E_n} \\
&= -\frac{1}{2} e^2 \mathcal{E}^2 \alpha. \qquad (5)
\end{aligned}
$$

The above equation serves to define the atomic polarizability α. From this equation, we obtain the general quantum mechanical expression for the atomic polarizability

$$
\alpha = 2 \sum_n \frac{\langle \Psi_v | \mathcal{Z} | \Psi_n \rangle \langle \Psi_n | \mathcal{Z} | \Psi_v \rangle}{E_n - E_v}. \qquad (6)
$$

In the usual approach, we determine wave functions for excited states Ψ_n and carry out the above sum over states. In the direct approach, we replace $H_{\rm ext} \to \mathcal{Z}$ and determine $\Psi_v^{(1)}$ by solving

$$
(H_0 + V - E_v) \Psi_v^{(1)} = -\mathcal{Z} \Psi_v \ . \qquad (7)
$$

We then find α using

$$
\alpha = -2 \langle \Psi_v | \mathcal{Z} | \Psi_v^{(1)} \rangle \ . \qquad (8)
$$

There are some tricky angular momentum questions that must be addressed as well as the unresolved question of scalar and tensor polarizabilities.

2 SD Method

One way to obtain accurate all-order wave functions is the SD method in which single and double excitations of the Hartree-Fock wave function $\Phi_v = a_v^\dagger |0\rangle$ are included to all orders in MBPT.

$$
\begin{aligned}
\Psi_v = \Bigg(1 &+ \sum_{am} \rho_{ma} \ a_m^\dagger a_a + \frac{1}{2} \sum_{abmn} \rho_{mnab} \ a_m^\dagger a_n^\dagger a_b a_a \\
&+ \sum_m \rho_{mv} \ a_m^\dagger a_v + \sum_{amn} \rho_{mnva} \ a_m^\dagger a_n^\dagger a_a a_v \Bigg) \Phi_v \ . \qquad (9)
\end{aligned}
$$

Let us consider the action of the operator $\mathcal{Z}$ on the SD wave function Ψ_v. We express the resultant wave function as

$$
\begin{aligned}
\mathcal{Z} \times \Psi_v = \Bigg(S \ a_v^\dagger &+ \sum_{am} \sigma_{ma} \ a_m^\dagger a_a a_v^\dagger + \frac{1}{2} \sum_{abmn} \sigma_{mnab} \ a_m^\dagger a_n^\dagger a_b a_a a_v^\dagger \\
&+ \sum_m \sigma_m \ a_m^\dagger + \sum_{amn} \sigma_{mna} \ a_m^\dagger a_n^\dagger a_a
\end{aligned}
$$

$$+ \sum_{abcmnr} \sigma_{mnrabc}\ a^\dagger_m a^\dagger_n a^\dagger_r a_a a_b a_c a^\dagger_v$$

$$\left. + \sum_{abmnr} \sigma_{mnrab}\ a^\dagger_m a^\dagger_n a^\dagger_r a_a a_b \right) |0\rangle \,. \qquad (10)$$

We find the following expressions for the excitation coefficients:

$$S = \sum_{am} z_{am} \rho_{ma} \qquad (11)$$

$$\sigma_{ma} = z_{ma} + \sum_n z_{mn} \rho_{na} - \sum_b z_{ba} \rho_{mb} + \sum_{nb} z_{bn} \left[\rho_{mnab} - \rho_{mnba}\right] \qquad (12)$$

$$\sigma_{mnab} = 2\ z_{nb} \rho_{ma} + \sum_r z_{mr} \left[\rho_{rnab} - \rho_{nrab}\right] + \sum_c z_{ca} \left[\rho_{mnbc} - \rho_{mncb}\right] \qquad (13)$$

$$\sigma_m = z_{mv} - \sum_a z_{av} \rho_{ma} + \sum_n z_{mn} \rho_{nv} + \sum_{an} z_{an} \left[\rho_{mnva} - \rho_{nmva}\right] \qquad (14)$$

$$\sigma_{mna} = z_{mv} \rho_{na} - z_{ma} \rho_{nv} + \sum_r z_{mr} \left[\rho_{rnva} - \rho_{nrva}\right] - \sum_b z_{ba} \rho_{mnvb} + \frac{1}{2} \sum_b z_{bv} \left[\rho_{mnab} - \rho_{mnba}\right] \qquad (15)$$

$$\sigma_{mnrabc} = \frac{1}{2} z_{ma} \rho_{nrcb} \qquad (16)$$

$$\sigma_{mnrab} = \frac{1}{2} z_{mv} \rho_{nrba} + z_{ma} \rho_{nrvb} \,. \qquad (17)$$

Now, we must find the corresponding expressions for $(H_0 + V - E_v)\Psi_v^{(1)}$ and match coefficients on left and right to obtain algebraic equations for the expansion coefficients. After these are obtained, one must consider the angular reduction. The $(JM) = (10)$ operator will lead to a state with angular momentum components $|j_v - 1| \leq j \leq j_v + 1$ and $m = m_v$. I would assume that we could drop triple excitations on the left and right of the inhomogeneous equation.

The form of Eq. (10) dictates the structure of the corresponding expansion for $\Psi_v^{(1)}$. On summing over magnetic substates, it is immediately obvious from (11) that $S = 0$, simplifying somewhat the expansion of the perturbed wave function.

3 Closed-Shell case

Let us consider first the simpler case of a closed-shell atom with no valence electron. We assume that the unperturbed wave function is given as an SD expansion:

$$\Psi_0 = \left(1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{abmn} \rho_{mnab}\ a_m^\dagger a_n^\dagger a_b a_a\right) |0\rangle\,, \tag{18}$$

and we expand the perturbed orbital correspondingly as

$$\Psi^{(1)} = \left(\sum_{ma} \tau_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{abmn} \tau_{mnab}\ a_m^\dagger a_n^\dagger a_b a_a\right) |0\rangle\,. \tag{19}$$

We find

$$\begin{aligned}
(H_0 + V - E)\Psi^{(1)} = &\left\{ \sum_{ma} \left[(\epsilon_m - \epsilon_a - \Delta E)\tau_{ma} + \sum_{bn} \tilde{g}_{mban}\tau_{nb} \right.\right. \\
&+ \left. \sum_{bnr} g_{mbnr}\tilde{\tau}_{nrab} - \sum_{bcn} g_{bcan}\tilde{\tau}_{mnbc} \right] a_m^\dagger a_a \\
&+ \frac{1}{2} \sum_{mnab} \left[(\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b - \Delta E)\,\tau_{mnab} + \sum_{cd} g_{cdab}\tau_{mncd} \right. \\
&+ \sum_{rs} g_{mnrs}\tau_{rsab} + \left(\sum_r g_{mnrb}\tau_{ra} - \sum_c g_{cnab}\tau_{mc} + \sum_{rc} \tilde{g}_{cnrb}\tilde{\tau}_{mrac} \right) \\
&+ \left. \left. \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right] a_m^\dagger a_n^\dagger a_b a_a \right\} |0\rangle\ .
\end{aligned} \tag{20}$$

It follows that

$$\begin{aligned}
(\epsilon_a - \epsilon_m + \Delta E)\tau_{ma} = &\sum_{bn} \tilde{g}_{mban}\tau_{nb} \\
&+ \sum_{bnr} g_{mbnr}\tilde{\tau}_{nrab} - \sum_{bcn} g_{bcan}\tilde{\tau}_{mnbc} + \sigma_{ma}
\end{aligned} \tag{21}$$

$$\begin{aligned}
(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n + \Delta E)\,\tau_{mnab} = &\sum_{cd} g_{cdab}\tau_{mncd} + \sum_{rs} g_{mnrs}\tau_{rsab} \\
&+ \left(\sum_r g_{mnrb}\tau_{ra} - \sum_c g_{cnab}\tau_{mc} + \sum_{rc} \tilde{g}_{cnrb}\tilde{\tau}_{mrac} \right) + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \\
&+ \sigma_{mnab}\ .
\end{aligned} \tag{22}$$

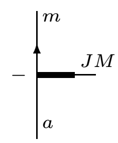
Now we must look at the angular structure.

3.1 Angular Decomposition

The perturbed wave function $\Psi^{(1)}$ has angular momentum (1,0). Coupling of particle-hole states is discussed on page 103 of the classroom notes and we follow that discussion below.

3.1.1 Single-Excitations

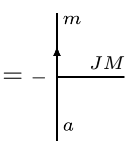
We expect that the single excitation terms $a^\dagger_m a_a|0\rangle$ will be coupled to (1,0). Following the notes, we find that combination



$$a^\dagger_m a_a|0\rangle$$

is a (J, M) angular momentum eigenstate. The extra factor $\sqrt{[J]}$ only affects the scale and can be dropped since the scale is determined by the inhomogeneous terms in the equation. We make the ansatz that the coefficients of the single-excitation terms have the form

$$\tau_{ma} = $$

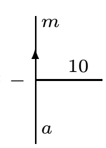


$$T(m, a) \ , \qquad (23)$$

where $T(m, a)$ is independent of magnetic quantum numbers. The resulting contribution to the wave function $\sum_{ma} \tau_{ma} a^\dagger_m a_a|0\rangle$ will then automatically be an angular momentum eigenstate.

The inhomogeneous driving term in the singles equation may be written in the required form as

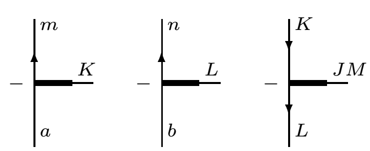
$$\sigma_{ma} = $$



$$\left\{ \langle m\|z\|a\rangle + \sum_n \langle m\|z\|n\rangle S(na)\delta_{\kappa_n\kappa_a} - \sum_b \langle b\|z\|a\rangle S(mb)\delta_{\kappa_b\kappa_m} + \sum_{nb} \frac{(-1)^{n+b}}{[1]} \langle b\|z\|n\rangle \tilde{S}_1(mnab) \right\} . \qquad (24)$$

3.1.2 Double Excitations

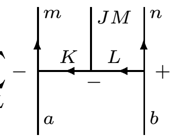
In a similar way, we can couple the two-particle two-hole state to angular momentum (JM) using



$$a^\dagger_m a^\dagger_n a_b a_a|0\rangle \ . \qquad (25)$$

Again, the factor $\sqrt{[J][K][L]}$ can be ignored since it merely affects scale. There are other possibilities also, but I believe that all other couplings can be reduced to this one using recouping coefficients that are independent of magnetic quantum numbers. We therefore assume that the double-excitation expansion coefficient may be written in the form

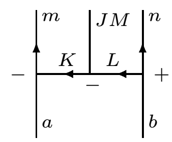
$$\tau_{mnab} = \sum_{KL}$$



$$T_{KL}(mnab) \qquad (26)$$

If we have a specific expression for τ_{mnab}, then we can find the corresponding expansion coefficients using the inversion formula:

$$T_{KL}(mnab) = [K][L][J] \sum_{\substack{m_m m_n \\ m_a m_b}}$$



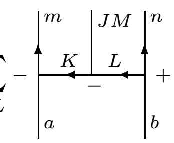
$$\tau_{mnab} \; . \qquad (27)$$

Symmetry under the transformation $\tau_{mnab} \leftrightarrow \tau_{nmba}$ implies that

$$T_{KL}(mnab) = (-1)^{L+K+1} \, T_{LK}(nmba) \; .$$

Let us represent the exchange term τ_{mnba} in the form:

$$\tau_{mnba} = \sum_{KL}$$



$$T^{\rm exc}_{KL}(mnab), \qquad (28)$$

then we find,

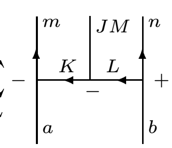
$$T^{\rm exc}_{KL}(mnab) = \sum_{RS} (-1)^{m+n+K+R} [K][L] \left\{ \begin{array}{ccc} a & m & K \\ n & b & L \\ S & R & 1 \end{array} \right\} T_{RS}(mnba) \; . \qquad (29)$$

The above function has the symmetry property

$$T^{\rm exc}_{KL}(mnab) = (-1)^{L+K+1} \, T^{\rm exc}_{LK}(nmba) \; .$$

Now we turn to the decomposition of σ_{mnab}. We write

$$\sigma_{mnab} = \sum_{KL}$$



$$Q_{KL}(mnab) \qquad (30)$$

Using the inversion formula, we find for the leading term

$$z_{nb}\rho_{ma} + z_{ma}\rho_{nb} \rightarrow \delta_{J1} \Big[\delta_{K0} \; \delta_{L1} \sqrt{[m][1]} \; \langle n \| z \| b \rangle \; S(ma) \; \delta_{\kappa_m \kappa_a} + \delta_{K1} \; \delta_{L0} \sqrt{[n][1]} \; \langle m \| z \| a \rangle \; S(nb) \; \delta_{\kappa_n \kappa_b} \Big] \; . \qquad (31)$$

For the second term in σ_{mnab} we find:

$$\frac{1}{2}\sum_r [z_{mr}\tilde{\rho}_{rnab} + z_{nr}\tilde{\rho}_{rmba}]$$
$$\rightarrow \frac{\delta_{J1}}{2}\sum_{rKL}\Bigg[(-1)^{L+J+a+m}[K]\left\{\begin{array}{ccc} K & L & 1 \\ r & m & a\end{array}\right\}\langle m||z||r\rangle\ \tilde{S}_L(rnab)$$
$$+ (-1)^{L+n+b}[L]\left\{\begin{array}{ccc} L & K & 1 \\ r & n & b\end{array}\right\}\langle n||z||r\rangle\ \tilde{S}_K(rmba)\Bigg] . \qquad (32)$$

For the third term, we find:

$$-\frac{1}{2}\sum_c [z_{ca}\tilde{\rho}_{mncb} + z_{cb}\tilde{\rho}_{nmca}]$$
$$\rightarrow -\frac{\delta_{J1}}{2}\sum_{cKL}\Bigg[(-1)^{K+a+m}[K]\left\{\begin{array}{ccc} K & L & 1 \\ c & a & m\end{array}\right\}\langle c||z||a\rangle\ \tilde{S}_L(mncb)$$
$$+ (-1)^{J+K+n+b}[L]\left\{\begin{array}{ccc} L & K & 1 \\ c & b & n\end{array}\right\}\langle c||z||b\rangle\ \tilde{S}_K(nmca)\Bigg] . \qquad (33)$$

3.1.3 Excited Singles Equation

Combining the above, we find that the singles coefficients satisfy

$$(\epsilon_a - \epsilon_m + \Delta E)T(ma) = \langle m\|z\|a\rangle$$
$$+ \sum_n \langle m\|z\|n\rangle S(na)\delta_{\kappa_n\kappa_a} - \sum_b \langle b\|z\|a\rangle S(mb)\delta_{\kappa_b\kappa_m} + \sum_{nb}\frac{(-1)^{n+b}}{[1]}\langle b\|z\|n\rangle \tilde{S}_1(mnab)$$
$$+ \sum_{bn}\frac{(-1)^{n+b}}{[1]}Z_1(mban)T(nb)$$
$$- \sum_{KLbnr}\frac{(-1)^{m+r+a+b+K}}{[L]}\left\{\begin{array}{ccc} K & L & 1 \\ m & a & n\end{array}\right\} Z_L(mbnr)T_{KL}(nrab)$$
$$- \sum_{KLbcn}\frac{(-1)^{m+n+a+c+L}}{[L]}\left\{\begin{array}{ccc} K & L & 1 \\ a & m & b\end{array}\right\} Z_L(bcan)T_{KL}(mnbc) . \qquad (34)$$

3.1.4 Excited Doubles Equation

We find the following contributions to doubles equations:

$$\sum_{cd} g_{cdab}\tau_{mncd} \rightarrow -\sum_{cdRSH}(-1)^{a+b+m+n+K+R+H}\ [K][L]\left\{\begin{array}{ccc} R & K & H \\ L & S & 1\end{array}\right\}\times$$
$$\left\{\begin{array}{ccc} R & K & H \\ a & c & m\end{array}\right\}\left\{\begin{array}{ccc} L & S & H \\ d & b & n\end{array}\right\} X_H(cdab)\ T_{RS}(mncd) . \qquad (35)$$

$$\sum_{mn} g_{mnrs}\tau_{rsab} \rightarrow -\sum_{mnRSH}(-1)^{a+b+m+n+S+L+H}\ [K][L]\left\{\begin{array}{ccc} R & K & H \\ L & S & 1\end{array}\right\}\times$$

$$\left\{\begin{array}{ccc} R & K & H \\ m & r & a \end{array}\right\}\left\{\begin{array}{ccc} L & S & H \\ s & n & b \end{array}\right\} X_H(mnrs)\; T_{RS}(rsab)\ . \quad (36)$$

$$\sum_r g_{mnrb}\tau_{ra} \rightarrow \sum_r (-1)^{a+m+K}\ [K]\left\{\begin{array}{ccc} K & L & 1 \\ r & a & m \end{array}\right\} X_L(mnrb)\; T(ra)\ . \quad (37)$$

$$-\sum_c g_{cnab}\tau_{mc} \rightarrow \sum_c (-1)^{a+m+L}\ [K]\left\{\begin{array}{ccc} K & L & 1 \\ c & m & a \end{array}\right\} X_L(cnab)\; T(mc)\ . \quad (38)$$

$$\sum_{rc} \tilde{g}_{cnrb}\tilde{\tau}_{mrac} \rightarrow -\sum_{KLrc} \frac{(-1)^{L+r+c}}{[L]} Z_L(cnrb)\; \tilde{T}_{KL}(mrac)\ , \quad (39)$$

where

$$\tilde{T}_{KL}(mnab) = T_{KL}(mnab) - T^{\rm exc}_{KL}(mnab)\ .$$

Putting all of this together, we may write

$$\begin{aligned}
&(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n + \Delta E)\; T_{KL}(mnab) = \\
&\quad \Bigg[\delta_{K0}\ \delta_{L1}\ \delta_{\kappa_m\kappa_a}\sqrt{[m][1]}\ \langle n\|z\|b\rangle\ S(ma) \\
&\quad -\frac{1}{2}\sum_r (-1)^{L+a+m}[K]\left\{\begin{array}{ccc} K & L & 1 \\ r & m & a \end{array}\right\}\langle m||z||r\rangle\ \tilde{S}_L(rnab) \\
&\quad -\frac{1}{2}\sum_c (-1)^{K+a+m}[K]\left\{\begin{array}{ccc} K & L & 1 \\ c & a & m \end{array}\right\}\langle c||z||a\rangle\ \tilde{S}_L(mncb) \\
&\quad -\sum_{cdRSH} (-1)^{a+b+m+n+K+R+H}\ [K][L]\left\{\begin{array}{ccc} R & K & H \\ L & S & 1 \end{array}\right\} \\
&\qquad\qquad \left\{\begin{array}{ccc} R & K & H \\ a & c & m \end{array}\right\}\left\{\begin{array}{ccc} L & S & H \\ d & b & n \end{array}\right\} X_H(cdab)\; T_{RS}(mncd) \\
&\quad -\sum_{mnRSH} (-1)^{a+b+m+n+S+L+H}\ [K][L]\left\{\begin{array}{ccc} R & K & H \\ L & S & 1 \end{array}\right\} \\
&\qquad\qquad \left\{\begin{array}{ccc} R & K & H \\ m & r & a \end{array}\right\}\left\{\begin{array}{ccc} L & S & H \\ s & n & b \end{array}\right\} X_H(mnrs)\; T_{RS}(rsab) \\
&\quad +\sum_r (-1)^{a+m+K}\ [K]\left\{\begin{array}{ccc} K & L & 1 \\ r & a & m \end{array}\right\} X_L(mnrb)\; T(ra) \\
&\quad +\sum_c (-1)^{a+m+L}\ [K]\left\{\begin{array}{ccc} K & L & 1 \\ c & m & a \end{array}\right\} X_L(cnab)\; T(mc) \\
&\quad -\sum_{KLrc} \frac{(-1)^{L+r+c}}{[L]} Z_L(cnrb)\; \tilde{T}_{KL}(mrac)\Bigg] + (-1)^{K+L+1}\left[\begin{array}{c} m \leftrightarrow n \\ a \leftrightarrow b \\ K \leftrightarrow L \end{array}\right].
\end{aligned} \quad (40)$$

3.2 Dipole Matrix Element

Now, we are faced with the problem of evaluating the dipole matrix element $\mathcal{M} = \langle \Psi_0 | \mathcal{Z} | \Psi^{(1)} \rangle$. We write:

$$\langle \Psi_0 | \mathcal{Z} | \Psi^{(1)} \rangle = \left\langle 0 \left| \left[1 + \sum_{ma} \rho^*_{ma} a^\dagger_a a_m + \sum_{mnab} \rho^*_{mnab} a^\dagger_a a^\dagger_b a_n a_m \right] \times \right. \right.$$

$$\left. \left. \sum_{ij} z_{ij}\ a^\dagger_i a_j \left[\sum_{rc} \tau_{rc}\ a^\dagger_r a_c + \sum_{rscd} \tau_{rscd}\ a^\dagger_r a^\dagger_s a_d a_c \right] \right| 0 \right\rangle . \quad (41)$$

We break this up into the sum of seven terms: $\mathcal{M} = \sum_{k=1}^{7} \mathcal{M}_k$, where

$$\mathcal{M}_1 = \sum_{cr} z_{cr} \tau_{rc} \quad (42)$$

$$\mathcal{M}_2 = \sum_{amr} \rho^*_{ma} z_{mr} \tau_{ra} \quad (43)$$

$$\mathcal{M}_3 = -\sum_{acm} \rho^*_{ma} z_{ca} \tau_{mc} \quad (44)$$

$$\mathcal{M}_4 = \sum_{abmn} \rho^*_{ma} z_{bn} \tilde{\tau}_{mnab} \quad (45)$$

$$\mathcal{M}_5 = \sum_{abmn} \tilde{\rho}^*_{mnab} z_{ma} \tau_{nb} \quad (46)$$

$$\mathcal{M}_6 = \frac{1}{2} \sum_{abmnr} \tilde{\rho}^*_{mnab} z_{mr} \tilde{\tau}_{rnab} \quad (47)$$

$$\mathcal{M}_7 = -\frac{1}{2} \sum_{abcmn} \tilde{\rho}^*_{mnab} z_{ca} \tilde{\tau}_{mncb} . \quad (48)$$

Additionally, the wave function Ψ_0 must be normalized. Since the matrix element depends quadratically on Ψ_0, the properly normalized matrix element is

$$\mathcal{M} = \frac{\sum_k \mathcal{M}_k}{\langle \Psi_0 | \Psi_0 \rangle} .$$

One also finds the following expression for the wave function norm:

$$\langle \Psi_0 | \Psi_0 \rangle = 1 + \sum_{ma} \rho^*_{ma} \rho_{ma} + \frac{1}{2} \sum_{mnab} \rho^*_{mnab} \tilde{\rho}_{mnab} . \quad (49)$$

3.2.1 Angular Decomposition of Matrix Element

Substituting the previously discussed angular momentum expansions for the perturbed and unperturbed wave functions into the expressions for the matrix element given above, we find

$$\mathcal{M}_1 = \frac{1}{[1]} \sum_{cr} \langle r \| z \| c \rangle\, T(rc) \quad (50)$$

$$\mathcal{M}_2 = \frac{1}{[1]} \sum_{amr} S(ma)\, \delta_{\kappa_m \kappa_a} \langle r \| z \| m \rangle \, T(ra) \tag{51}$$

$$\mathcal{M}_3 = -\frac{1}{[1]} \sum_{acm} S(ma)\, \delta_{\kappa_m \kappa_a} \langle a \| z \| c \rangle \, T(mc) \tag{52}$$

$$\mathcal{M}_4 = \sum_{abmn} \sqrt{\frac{[m]}{[1]^3}}\, S(ma)\, \delta_{\kappa_m \kappa_a} \langle n \| z \| b \rangle \, \tilde{T}_{01}(mnab) \tag{53}$$

$$\mathcal{M}_5 = -\frac{1}{[1]^2} \sum_{abmn} \tilde{S}_1(mnab)\, \langle m \| z \| a \rangle \, T(nb) \tag{54}$$

$$\mathcal{M}_6 = \frac{1}{2} \sum_{abmnrKL} \frac{(-1)^{m-a+L}}{[1][L]} \left\{ \begin{array}{ccc} K & L & 1 \\ m & r & a \end{array} \right\} \times \tag{55}$$

$$\tilde{S}_L(mnab)\, \langle m \| z \| r \rangle \, \tilde{T}_{KL}(rnab) \tag{56}$$

$$\mathcal{M}_7 = -\frac{1}{2} \sum_{abcmnKL} \frac{(-1)^{m-a+K}}{[1][L]} \left\{ \begin{array}{ccc} K & L & 1 \\ a & c & m \end{array} \right\} \times \tag{57}$$

$$\tilde{S}_L(mnab)\, \langle c \| z \| a \rangle \, \tilde{T}_{KL}(mncb). \tag{58}$$

The angular-momentum decomposition of the wave function norm is also easily obtained as

$$\langle \Psi_0 | \Psi_0 \rangle = 1 + \sum_{ma} [a] S(ma)^2 \delta_{\kappa_m \kappa_a} + \frac{1}{2} \sum_{mnabL} \frac{1}{[L]} \tilde{S}_L(mnab) S_L(mnab). \tag{59}$$

3.2.2 Lowest-Order Perturbation Theory

Let us consider the MBPT expansion of $\mathcal{M}$. From the basic equations, it is clear that in lowest order only the single-excitation contribution to the perturbed wave function survives. Moreover,

$$T^{(0)}(ma) = \frac{\langle m \| z \| a \rangle}{\epsilon_a - \epsilon_m + \Delta E} \ . \tag{60}$$

In lowest order, only $\mathcal{M}_1$ contributes to the matrix element. Therefore,

$$\mathcal{M}^{(0)} = \frac{1}{[1]} \sum_{cr} \langle r \| z \| c \rangle \, T^{(0)}(rc) = \frac{1}{[1]} \sum_{cr} \frac{\langle r \| z \| c \rangle^2}{\epsilon_c - \epsilon_r + \Delta E} \ . \tag{61}$$

It follows that the polarizability is given in lowest order by

$$\alpha^{(0)} = \frac{2}{3} \sum_{cr} \frac{\langle r \| z \| c \rangle^2}{\epsilon_r - \epsilon_c - \Delta E} \ , \tag{62}$$

which is , aside from the ΔE in the denominator, just the HF expression for the polarizability of a closed-shell atom.