Theoretical details of application of Coupled-cluster theory to the Atomic EDMs of closed-shell atoms

K.V.P. Latha
Indian Institute of Astrophysics, Bangalore

Angom Dilip
Physical Research Laboratory, Ahmedabad

25th December 2004

Contents

1 Introduction to coupled-cluster theory **5**

2 Coupled-cluster equations: **5**
2.1 Linear equations : 5

3 H_{EDM} perturbed coupled-cluster equations **6**
3.1 Linearised H_{EDM} perturbed coupled-cluster equations 7
3.2 Non-linear H_{EDM} perturbed coupled-cluster equations 10

4 Derivation of Coupled-cluster equations by a different approach **15**

5 Coupled-cluster equations in terms of E_{corr} **16**

6 H_{EDM} perturbed Coupled-cluster equations for singles **17**

7 Connection between CI, MBPT and CCT. **23**

8 Selection rules of H_{EDM} perturbed cluster amplitudes : **26**

9 The tensor-pseudotensor H_{EDM} matrix element **29**

10 Calculation of the H_{PTV} matrix elements **32**

List of Figures

3.1.1 Notation for diagrams 8
3.1.2 Diagrams contributing to $T_1^{(1)}$ in C-matrix 8
3.1.3 Diagrams contributing to $T_1^{(1)}$ in A-matrix 9
3.2.1 Diagrams contributing to $T_1^{(1)}$ in A-matrix(non-linear) 12
3.2.2 Diagrams contributing to $T_1^{(1)}$ in A-matrix(non-linear) 13
3.2.3 Diagrams contributing to $T_1^{(1)}$ 14
3.2.4 Diagrams contributing to $T_1^{(1)}$ 15
6.0.1 Diagram representing $V_N T_2^{(0)} T_2^{(0)}$ 19
6.0.2 Notation for interaction lines 20
6.0.3 Contribution of $\bar{f}_N T^{(1)}$ and $\bar{V}_N T^{(1)}$ to singles 21
6.0.4 Contribution of $\bar{f}_N T^{(1)}$ and $\bar{V}_N T^{(1)}$ to doubles 22
6.0.5 Contribution of $\bar{f}_N$ and $\bar{V}_N$ to singles 23
6.0.6 Contribution of $\bar{f}_N$ and $\bar{V}_N$ to doubles 23
7.0.1 Unperturbed cluster operators 25
8.0.1 Diagram representing $T_1^{(1)}$ 27
8.0.2 Diagram representing $T_2^{(1)}$ 27

List of Tables

1 Introduction to coupled-cluster theory

The Dirac-Coulomb Hamiltonian of an atomic system is,

$$H = \sum_i \left[c\boldsymbol{\alpha_i} \cdot .\boldsymbol{p_i} + \beta_i mc^2 + V(r_i)\right] + \sum_{i<j} \frac{1}{r_{ij}} \tag{1.0.1}$$

where, c is velocity of light, α and β are the Dirac matrices, m is the mass of electron r_{ij} is the Coulomb potential energy between two electrons, in atomic units. Let $|\Psi\rangle$ represents an exact eigen state of the above Hamiltonian, and let $|\Phi_0\rangle$ represents the ground state of the atomic system and is fixed.Then,

$$|\Psi\rangle = \Omega|\Phi_0\rangle \tag{1.0.2}$$

where Ω is the wave operator. In coupled cluster theory, the wave operator $\Omega = e^T$, where T is an operator and $T = \sum_i T_i$ where T_i are cluster operators which excite i electrons from occupied to virtual shells with respect to the reference state $|\Phi_0\rangle$. Hence,

$$|\Psi\rangle = e^T|\Phi_0\rangle \tag{1.0.3}$$

2 Coupled-cluster equations:

2.1 Linear equations :

The Schroedinger equation of the Dirac-Coulomb Hamiltonian is

$$H|\Psi\rangle = E|\Psi\rangle \Rightarrow He^T|\Phi_0\rangle = Ee^T|\Phi_0\rangle$$

Operating from left side by e^{-T}

$$e^{-T}He^T|\Phi_0\rangle = E|\Phi_0\rangle$$

Expressing H in normal ordered form,$H = H_N^0 + E_{HF}$ Then,

$$e^{-T}(H_N^0 + E_{HF})e^T|\Phi_0\rangle = E|\Phi_0\rangle \tag{2.1.1}$$

Projecting Eq.2.1.1 with singly and doubly excited states $\langle\Phi_a^r|$ and $\langle\Phi_{ab}^{rs}|$ and restricting T to $T = T_1 + T_2$, the single and double excitation cluster amplitude equations are obtained. Expanding $e^{-T}H_N^0e^T$ using Campbell-Baker-Hausdorf expansion

$$e^{-T}H_N^0e^T = H_N^0 + \left[H_N^0, T\right] + \frac{1}{2!}\left[\left[H_N^0, T\right], T\right] + \frac{1}{3!}\left[\left[\left[H_N^0, T\right], T\right], T\right] + \frac{1}{4!}\left[\left[\left[\left[H_N^0, T\right], T\right], T\right], T\right]$$

Using $[H_N^0, T] = \left\{\widehat{H_N^0 T}\right\} - \left\{\widehat{TH_N^0}\right\}$ and $\left\{\widehat{TH_N^0}\right\} = 0$ we get,

$$e^{-T}H_N^0e^T = H_N^0 + \left\{\widehat{H_N^0 T}\right\} + \left\{\widehat{H_N^0 TT}\right\} + \left\{\widehat{H_N^0 TTT}\right\} + \left\{\widehat{H_N^0 TTTT}\right\} \tag{2.1.2}$$

Substituting the above in Eq.2.1.1 and retaining only the terms linear in T,

$$\langle \Phi_a^r | \left\{ H_N^0 + \widehat{H_N^0 T} \right\} | \Phi_0 \rangle = 0 \quad (2.1.3)$$

$$\langle \Phi_{ab}^{rs} | \left\{ H_N^0 + \widehat{H_N^0 T} \right\} | \Phi_0 \rangle = 0 \quad (2.1.4)$$

Since we use the approximation $T = T_1 + T_2$,

$$\langle \Phi_a^r | H_N^0 | \Phi_0 \rangle + \langle \Phi_a^r | \left\{ (\widehat{H_N^0 T_1} + \widehat{H_N^0 T_2}) \right\} | \Phi_0 \rangle = 0 \quad (2.1.5)$$

$$\langle \Phi_{ab}^{rs} | H_N^0 | \Phi_0 \rangle + \langle \Phi_{ab}^{rs} | \left\{ (\widehat{H_N^0 T_1} + \widehat{H_N^0 T_2}) \right\} | \Phi_0 \rangle = 0 \quad (2.1.6)$$

The above equations can be written in the form,

$$H_{11} T_1 + H_{12} T_2 = -H_{10} \quad (2.1.7)$$

$$H_{21} T_1 + H_{22} T_2 = -H_{20} \quad (2.1.8)$$

Combining the equations,

$$\mathbf{A} T = \mathbf{C} \quad (2.1.9)$$

where $\mathbf{A}$ and $\mathbf{C}$ are independent of T. This is a linear matrix equation.

By expanding $e^{-T} H_N^0 e^T$ to higher orders in T a non-linear matrix equation can be obtained, which is of the form,

$$\mathbf{A}(T) T = \mathbf{C} \quad (2.1.10)$$

which should be solved in a self-consistent way to obtain the unperturbed cluster amplitudes.

3 H_{EDM} perturbed coupled-cluster equations

Let $|\Psi'\rangle$ be the H_{EDM} perturbed exact state of the atomic Hamiltonian given in Section I. Then,

$$|\Psi'\rangle = \Omega |\Phi_0'\rangle \quad (3.0.1)$$

where $|\Phi_0'\rangle$ is the perturbed reference state . Then,

$$|\Psi'\rangle = \Omega |\Phi_0'\rangle = e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle \quad (3.0.2)$$

Using

$$\left[T^{(0)}, T^{(1)} \right] = \left\{ \widehat{T^{(0)}, T^{(1)}} \right\} - \left\{ \widehat{T^{(1)}, T^{(0)}} \right\} = 0$$

we get

$$= e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle$$

where $T^{(1)}$ is the H_{EDM} perturbed cluster operator and λ is the perturbation parameter. The perturbed Schroedinger equation is,

$$H' e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle = E e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle$$

where $H' = H + \lambda H_{EDM}$. Define the normal ordered form of $H_N' = H_N^0 + \lambda H_{EDM}^N$.

3.1 Linearised H_{EDM} perturbed coupled-cluster equations

Similar to the unperturbed singles and doubles cluster amplitudes equations, the H_{EDM} perturbed singles and doubles cluster amplitudes equations are,

$$\langle \Phi_a^{r\prime} | \left\{ H'_N + \widehat{H'_N T'} \right\} |\Phi_0\rangle = 0 \quad (3.1.1)$$

$$\langle \Phi_{ab}^{rs\prime} | \left\{ H'_N + \widehat{H'_N T'} \right\} |\Phi_0\rangle = 0 \quad (3.1.2)$$

where $T' = T^{(0)} + \lambda T^{(1)}$ and $|\Phi_a^{r\prime}\rangle$ and $|\Phi_{ab}^{rs\prime}\rangle$ are the singly and doubly excited states. The projected states $|\Phi_a^{r\prime}\rangle$ and $|\Phi_{ab}^{rs\prime}\rangle$ are opposite in parity compared to $|\Phi_0\rangle$ since H_{EDM} is odd under parity. The single excitation equation is,

$$\langle \Phi_a^{r\prime} | H_N^0 + \lambda H_{EDM}^N | \Phi_0\rangle + \langle \Phi_a^{r\prime} | \left\{ (\widehat{H_N^0 T^{(0)}} + \lambda \widehat{H_N^0 T^{(1)}} + \lambda \widehat{H_{EDM}^N T^{(0)}} + \lambda^2 \widehat{H_{EDM}^N T^{(1)}} \right\} |\Phi_0\rangle = 0$$

Retaining terms linear in λ,

$$\langle \Phi_a^{r\prime} | \left\{ H_{EDM}^N + \widehat{H_{EDM}^N T^{(0)}} \right\} |\Phi_0\rangle + \langle \Phi_a^{r\prime} | \left\{ \widehat{H_N^0 T_1^{(1)}} + \widehat{H_N^0 T_2^{(1)}} \right\} |\Phi_0\rangle = 0$$

Expanding $T^{(0)}$ and $T^{(1)}$ as

$$T^{(0)} = T_1^{(0)} + T_2^{(0)}$$

and

$$T^{(1)} = T_1^{(1)} + T_2^{(1)},$$

and rearranging the equation

$$\langle \Phi_a^{r\prime} | \left\{ \widehat{H_N^0 T_1^{(1)}} \right\} |\Phi_0\rangle + \langle \Phi_a^{r\prime} | \left\{ \widehat{H_N^0 T_2^{(1)}} \right\} |\Phi_0\rangle = -(\langle \Phi_a^{r\prime} | \left\{ \widehat{H_{EDM}^N T_1^{(0)}} \right\} |\Phi_0\rangle$$

$$+ \langle \Phi_a^{r\prime} | \left\{ \widehat{H_{EDM}^N T_2^{(0)}} \right\} |\Phi_0\rangle + \langle \Phi_a^{r\prime} | H_{EDM}^N | \Phi_0\rangle) \quad (3.1.3)$$

The above equation can be cast in the form of a linear matrix equation,

$$H_{11} T_1^{(1)} + H_{12} T_2^{(1)} = -H'_{10} T_1^{(0)} - H'_{10} T_2^{(0)} - H_{10} \quad (3.1.4)$$

Similarly double excitations satisfy the equation,

$$H_{21} T_1^{(1)} + H_{22} T_2^{(1)} = -H'_{20} T_1^{(0)} - H'_{20} T_2^{(0)} - H_{20} \quad (3.1.5)$$

This is a linear matrix equation which can be written in the form,

$$\mathbf{A}T = \mathbf{C} \quad (3.1.6)$$

where $\mathbf{A}$ and $\mathbf{C}$ are independent of T. The diagrams contributing to $T_1^{(1)}$ in the linear approximation are shown in Fig.3.1.2 and Fig.3.1.3.

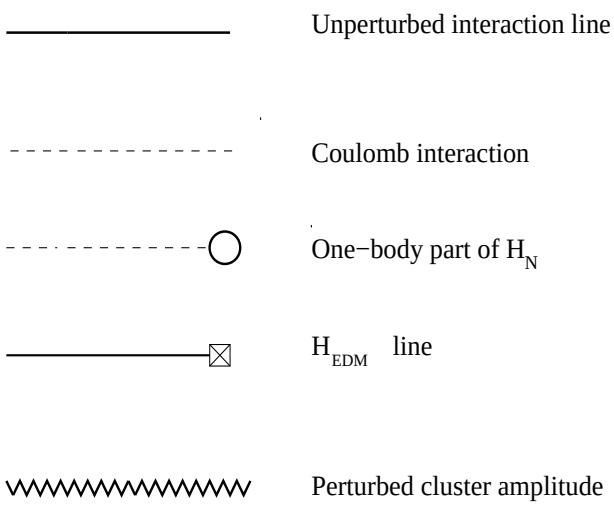

Figure 3.1.1: Notation for diagrams

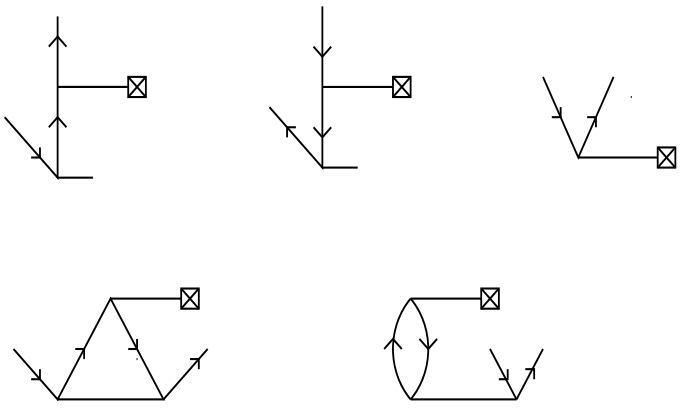

Figure 3.1.2: Diagrams contributing to $T_1^{(1)}$ in C-matrix

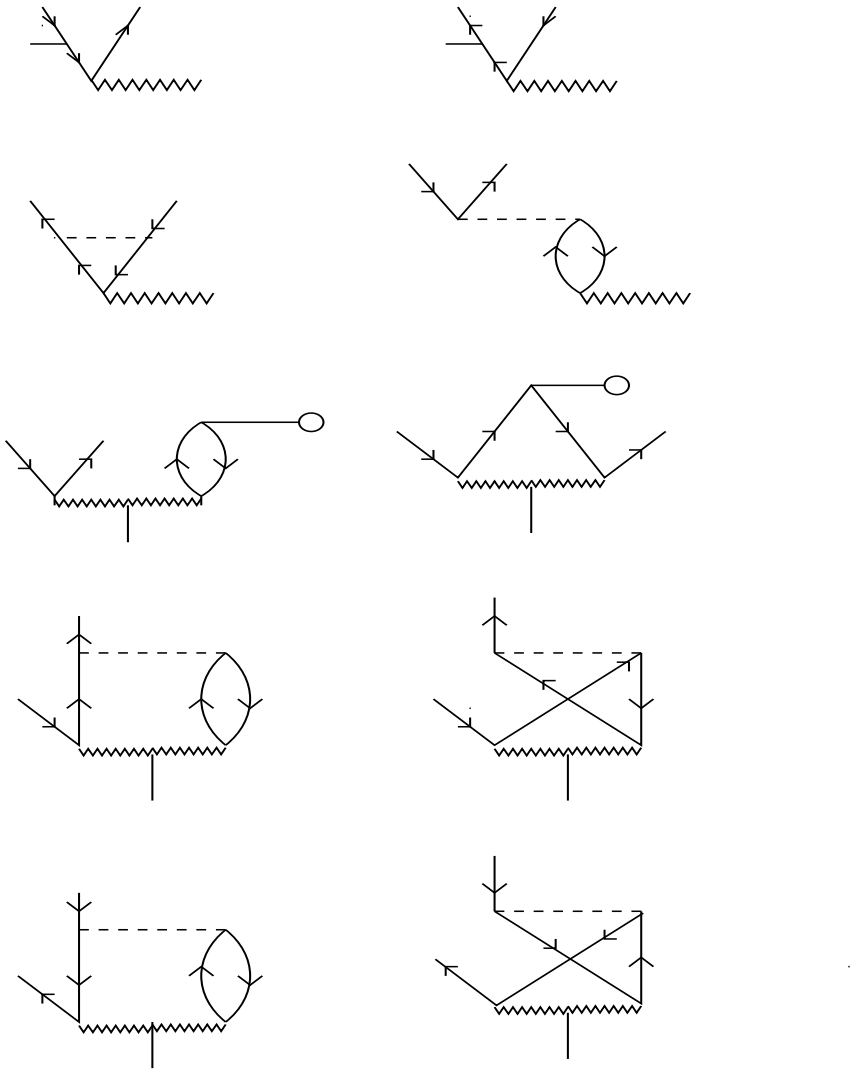

Figure 3.1.3: Diagrams contributing to $T_1^{(1)}$ in A-matrix

3.2 Non-linear H_{EDM} perturbed coupled-cluster equations

Consider the H_{EDM} perturbed singles and doubles cluster amplitudes equation

$$\langle \Phi_a^{r\prime}| \left\{ H'_N + \widehat{H'_N T'} \right\} |\Phi_0\rangle = 0 \qquad (3.2.1)$$

$$\langle \Phi_{ab}^{rs\prime}| \left\{ H'_N + \widehat{H'_N T'} \right\} |\Phi_0\rangle = 0 \qquad (3.2.2)$$

Including the terms non-linear in T'

$$\langle \Phi_a^r| H'_N + \left\{ \widehat{H'_N T'} + \frac{1}{2!}\widehat{H'_N T' T'} + \frac{1}{3!}\widehat{H'_N T' T' T'} + \frac{1}{4!}\widehat{H'_N T' T' T' T'} \right\} |\Phi_0\rangle = 0 \qquad (3.2.3)$$

and substituting $H'_N = H_N^0 + \lambda H_{EDM}^N$ and $T' = T^{(0)} + \lambda T^{(1)}$, the equation for single excitations reduces to

$$\langle \Phi_a^{r\prime}| H_{EDM}^N |\Phi_0\rangle + \langle \Phi_a^{r\prime}| \left\{ \widehat{H_N^0 T_1^{(1)}} + \widehat{H_N^0 T_2^{(1)}} + \widehat{H_{EDM}^N T_1^{(0)}} + \widehat{H_{EDM}^N T_2^{(0)}} + \widehat{H_N^0 T_1^{(0)}} + \widehat{H_N^0 T_2^{(0)}} \right\} +$$

$$\frac{1}{2!}\left[\left\{ \widehat{2H_N^0 T_1^{(0)}} T_1^{(1)} + \widehat{2H_N^0 T_1^{(0)}} T_2^{(1)} + \widehat{2H_N^0 T_2^{(0)}} T_1^{(1)} + \widehat{H_N^{EDM} T_1^{(0)}} T_1^{(0)} \right\} \right] +$$

$$\frac{1}{3!}\left[\left\{ \widehat{3H_N^0 T_1^{(0)} T_1^{(0)}} T_1^{(1)} \right] \right\} |\Phi_0\rangle = 0$$

The double excitations satisfy the equation

$$\langle \Phi_{ab}^{rs\prime}| H_{EDM}^N |\Phi_0\rangle + \langle \Phi_{ab}^{rs\prime}| \left\{ \widehat{H_N^0 T_1^{(1)}} + \widehat{H_N^0 T_2^{(1)}} + \widehat{H_N^{EDM} T_2^{(0)}} \right\} \qquad (3.2.4)$$

$$+\frac{1}{2!}\left[\left\{ \widehat{2H_N^0 T_1^{(0)}} T_1^{(1)} + \widehat{2H_N^0 T_1^{(0)}} T_2^{(1)} + \widehat{2H_N^0 T_2^{(0)}} T_1^{(1)} + \widehat{2H_N^0 T_2^{(0)}} T_2^{(1)} + \widehat{2H_N^{EDM} T_1^{(0)}} T_2^{(0)} \right\} \right] +$$

$$\frac{1}{3!}\left[\left\{ \widehat{3H_N^0 T_1^{(0)} T_1^{(0)}} T_1^{(1)} + \widehat{6H_N^0 T_1^{(0)} T_2^{(0)}} T_1^{(1)} + \widehat{3H_N^0 T_1^{(0)} T_2^{(1)}} T_1^{(0)} \right\} \right] +$$

$$\frac{1}{4!}\left[\left\{ \widehat{4H_N^0 T_1^{(0)} T_1^{(0)} T_1^{(0)}} T_1^{(1)} \right\} \right] |\Phi_0\rangle = 0$$

writing the equation for singles in terms of matrix elements,

$$\mathbf{A}_1(T^{(0)}) T_1^{(1)} + \mathbf{B}_1(T^{(0)}) T_2^{(1)} = \mathbf{C}_1(T^{(0)}) T_1^{(0)} + \mathbf{D}_1 T_2^{(0)} - (H_{EDM}^N)_0^1 \qquad (3.2.5)$$

where

$$\mathbf{A}_1(T) T_1^{(1)} = \langle \Phi_a^{r\prime}| \left\{ \widehat{H_N^0 T_1^{(1)}} + \frac{2}{2!}\left[\widehat{H_N^0 T_1^{(0)}} T_1^{(1)} + \widehat{H_N^0 T_2^{(0)}} T_1^{(1)} \right] + \frac{3}{3!}\left[\widehat{H_N^0 T_1^{(0)} T_1^{(0)}} T_1^{(1)} \right] \right\} |\Phi_0\rangle$$

which can be written as

$$\mathbf{A}_1(T) = (H^1)^1_1 + \frac{2}{2!}(H^1)^{01}_{11} + \frac{2}{2!}(H^1)^{01}_{21} + \frac{3}{3!}(H^1)^{001}_{111},$$

Similarly

$$\mathbf{B}_1 T_2^{(1)} = \langle \Phi_a^{r\prime} | \left\{ \widehat{H_N^0 T_2^{(1)}} \right\} | \Phi_0 \rangle$$

can be written as

$$\mathbf{B}_1 = (H^1)^1_2,$$

$$\mathbf{C}_1(T) T_1^{(0)} = \langle \Phi_a^{r\prime} | \left\{ \widehat{H_{EDM}^N} T_1^{(0)} + \frac{2}{2!} \left[\widehat{H_N^0 T_2^{(1)}} T_1^{(0)} \right] + \widehat{H_{EDM}^N T_1^{(0)}} T_1^{(0)} \right\} | \Phi_0 \rangle$$

can be written as

$$\mathbf{C}_1(T) = ({H_{EDM}^N}^1)^1_0 + \frac{2}{2!} \left[(H^1)^{10}_{21} \right] + ({H_{EDM}^N}^1)^{00}_{11},$$

$$\mathbf{D}_1 T_2^{(0)} = \langle \Phi_a^{r\prime} | \widehat{H_{EDM}^N T_2^{(0)}} | \Phi_0 \rangle$$

can be written as

$$\mathbf{D}_1 = \langle \Phi_a^{r\prime} | \widehat{H_{EDM}^N T_2^{(0)}} | \Phi_0 \rangle.$$

Similarly for the double-excitations,

$$\mathbf{A}_2(T) T_2^{(1)} + \mathbf{B}_2(T) T_1^{(1)} = \mathbf{C}_2(T) T_2^{(0)} + \mathbf{D}_2(T) T_1^{(0)} - (H_{EDM})^2_0 \qquad (3.2.6)$$

These equations are non-linear in $T^{(0)}$, but linear in $T^{(1)}$ and can be expressed as

$$\mathbf{A}(T^{(0)}) T^{(1)} = \mathbf{C} \qquad (3.2.7)$$

which can be solved iteratively, to get the perturbed cluster amplitudes, where the $T^{(0)}$ amplitudes are known. Splitting the matrix $\mathbf{A}(T^{(0)})$ in the above equation into diagonal and off-diagonal parts,

$$\mathbf{A}_{diag}(T^{(0)}) T^{(1)} + \mathbf{A}_{offdiag}(T^{(0)}) T^{(1)} = \mathbf{C}$$

gives an equation of the form

$$T^{(1)} = \frac{1}{\mathbf{A}_{diag}(T)} \left[\mathbf{C} - \mathbf{A}_{offdiag}(T) T^{(1)} \right] \qquad (3.2.8)$$

This equation has to be solved self-consistently where $T^{(1)}$'s are the unknowns.

The diagrams contributing to $T_1^{(1)}$ from the non-linear $T^{(0)}$ terms are shown in Fig.3.2.1.

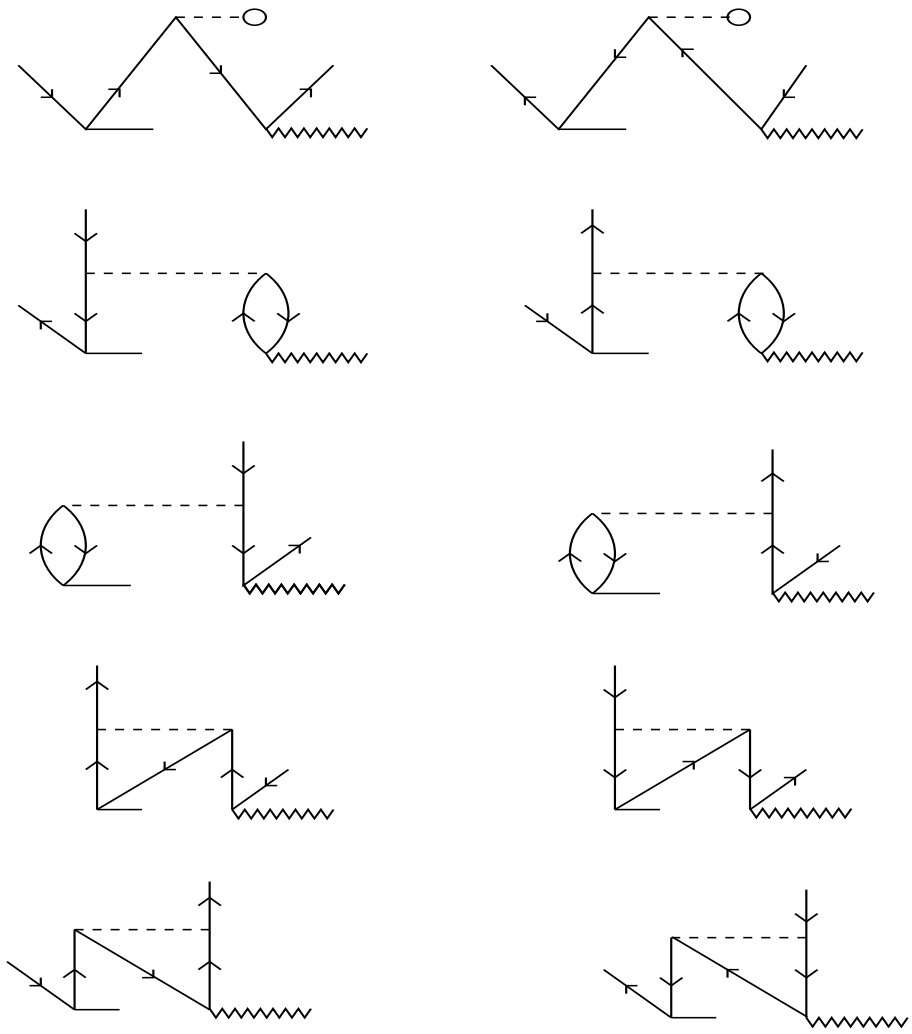

Figure 3.2.1: Diagrams contributing to $T_1^{(1)}$ in A-matrix(non-linear)

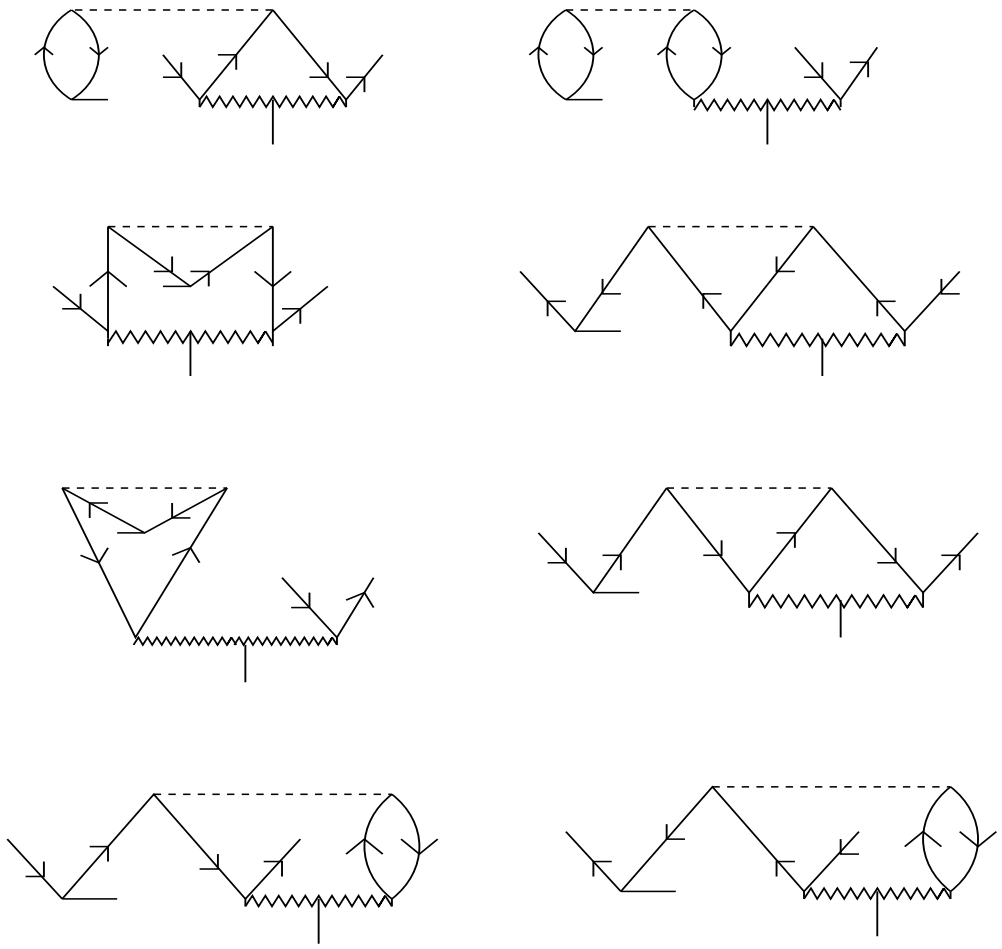

Figure 3.2.2: Diagrams contributing to $T_1^{(1)}$ in A-matrix(non-linear)

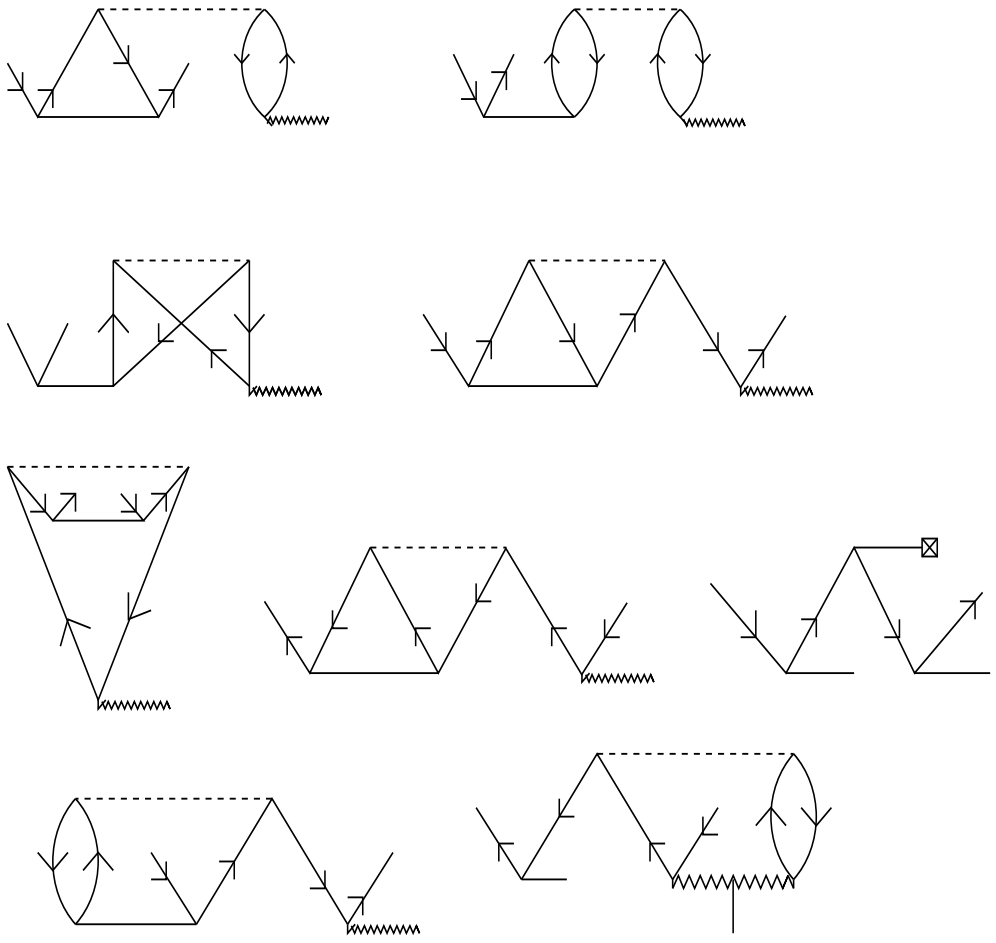

Figure 3.2.3: Diagrams contributing to $T_1^{(1)}$

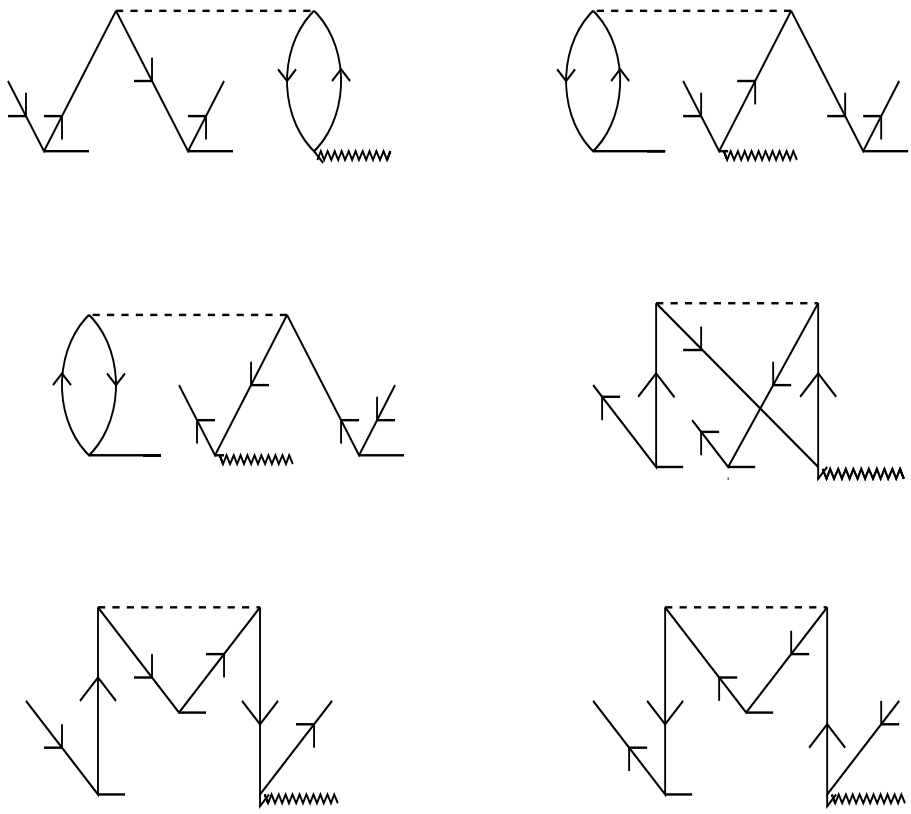

Figure 3.2.4: Diagrams contributing to $T_1^{(1)}$

4 Derivation of Coupled-cluster equations by a different approach

Consider the H_{EDM} perturbed Schroedinger equation

$$H|\Psi\rangle = E|\Psi\rangle \tag{4.0.1}$$

where $H = H_a + \lambda H_{EDM}$ and $|\Psi\rangle = e^T|\Phi_0\rangle = e^{T^{(0)}+\lambda T^{(1)}}|\Phi_0\rangle$. Since terms of one order in λ are taken, this gives,

$$He^{T^{(0)}}\left(1+\lambda T^{(1)}\right)|\Phi_0\rangle = Ee^{T^{(0)}}\left(1+\lambda T^{(1)}\right)|\Phi_0\rangle$$

Substituting $H = H_a + \lambda H_{EDM}$,

$$H = \left(H_a + \lambda H_{EDM}\right)e^{T^{(0)}}\left(1+\lambda T^{(1)}\right)|\Phi_0\rangle = Ee^{T^{(0)}}\left(1+\lambda T^{(1)}\right)|\Phi_0\rangle$$

Comparing λ^0 and λ^1 terms on both sides,

$$H_a e^{T^{(0)}}|\Phi_0\rangle = Ee^{T^{(0)}}|\Phi_0\rangle \tag{4.0.2}$$

and

$$\left(H_a e^{T^{(0)}} T^{(1)} + H_{EDM} e^{T^{(0)}}\right) |\Phi_0\rangle = E e^{T^{(0)}} T^{(1)} |\Phi_0\rangle \tag{4.0.3}$$

Multiplying Eq.4.0.2 by $T^{(1)}$,

$$T^{(1)} H_a e^{T^{(0)}} |\Phi_0\rangle = E T^{(1)} e^{T^{(0)}} |\Phi_0\rangle \tag{4.0.4}$$

Using the normal-ordered form of $H_a = H_a^N + E_{DF}$, Eq.4.0.3 becomes,

$$\left(H_a^N e^{T^{(0)}} T^{(1)} + H_{EDM} e^{T^{(0)}}\right) |\Phi_0\rangle = \left(\Delta E_{corr} e^{T^{(0)}} T^{(1)}\right) |\Phi_0\rangle \tag{4.0.5}$$

since $T^{(0)}$ and $T^{(1)}$ commute. Operating by $e^{-T^{(0)}}$ and subtracting Eq.4.0.5 from Eq.4.0.4,

$$\left[\bar{H}_a^N, T^{(1)}\right] |\Phi_0\rangle = -\bar{H}_{EDM} |\Phi_0\rangle \tag{4.0.6}$$

where $\bar{O} = e^{-T^{(0)}} \hat{O} e^{T(0)}$ where $\hat{O}$ is any operator. The equation for the Coupled-cluster singles and doubles can be derived from the basic equation, Eq.4.0.6.

5 Coupled-cluster equations in terms of E_{corr}

Consider the H_{EDM} perturbed Schroedinger equation,

$$H|\Psi\rangle = E|\Psi\rangle$$

$$H e^T |\Phi_0\rangle = E e^T |\Phi_0\rangle$$

$$H e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle = E e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle$$

$$\left(H_a + \lambda H_{EDM}\right) e^{T^{(0)}} \left(1 + \lambda T^{(1)}\right) |\Phi_0\rangle = E e^{T^{(0)}} \left(1 + \lambda T^{(1)}\right) |\Phi_0\rangle$$

Using the normal ordered form of H_a and operating throughout by $e^{-T^{(0)}}$ this equation becomes,

$$\left(H_a^N T^{(1)} + H_{EDM}\right) |\Phi_0\rangle = \Delta E_{corr} T^{(1)} |\Phi_0\rangle \tag{5.0.1}$$

· Rajat suggested the following way to obtain same equations:

Start from the H_{EDM} perturbed Schroedinger equation,

$$H|\Psi\rangle = E|\Psi\rangle = e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle$$

Expressing H in normal ordered form, $H = H_N + E_{DF}$ where $H_N = H_0^N + \lambda H_{EDM}^N$. Substituting H and $|\Psi\rangle$ in the Schroedinger equation,

$$\left[H_0^N + \lambda H_{EDM} + E_{DF}\right] e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle = E e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle$$

$$\left[H_0^N + \lambda H_{EDM}\right] e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle = (E - E_{DF})\, e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle$$
$$= \Delta E_{corr} e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle$$

Pre-multiplying by $e^{-T^{(0)}}$,

$$e^{-T^{(0)}} \left[H_0^N + \lambda H_{EDM}\right] e^{T^{(0)}} e^{\lambda T^{(1)}} |\Phi_0\rangle = \Delta E_{corr} e^{\lambda T^{(1)}} |\Phi_0\rangle$$

Again pre-multiplying by $e^{-\lambda T^{(1)}}$,

$$\left[e^{-\lambda T^{(1)}} \bar{H}_0^N e^{\lambda T^{(1)}} + e^{-\lambda T^{(1)}} \bar{H}_{EDM} e^{\lambda T^{(1)}}\right] |\Phi_0\rangle = \Delta E_{corr} |\Phi_0\rangle$$

Expanding the quantities within the square brackets,

$$\left(\bar{H}_0^N + \left[\bar{H}_0^N, \lambda T^{(1)}\right] + ... + \lambda \bar{H}_{EDM} + \lambda \left[\bar{H}_{EDM}, \lambda T^{(1)}\right] + ...\right) |\Phi_0\rangle = \Delta E_{corr} |\Phi_0\rangle$$

Now equating the powers of λ,

- $$\bar{H}_0^N |\Phi_0\rangle = \Delta E_{corr} |\Phi_0\rangle$$
- $$\left[\bar{H}_0^N, \lambda T^{(1)}\right] |\Phi_0\rangle + \lambda \bar{H}_{EDM} |\Phi_0\rangle = 0.$$

The second equation gives,

$$\left[\bar{H}_0^N, T^{(1)}\right] |\Phi_0\rangle = -\bar{H}_{EDM} |\Phi_0\rangle \tag{5.0.2}$$

6 H_{EDM} perturbed Coupled-cluster equations for singles

Consider the determining equation for singles,

$$\langle \Phi_a^{r\prime}| \left[\bar{H_a^N}, T^{(1)}\right] |\Phi_0\rangle = -\langle \Phi_a^{r\prime}| \bar{H}_{EDM} |\Phi_0\rangle \tag{6.0.1}$$

$$\langle \Phi_a^{r\prime}| \{\widehat{\bar{H_a^N} T^{(1)}}\} |\Phi_0\rangle - \langle \Phi_a^{r\prime}| \{\widehat{T^{(1)} \bar{H_a^N}}\} |\Phi_0\rangle = -\langle \Phi_a^{r\prime}| \bar{H}_{EDM} |\Phi_0\rangle$$

Substituting for $\bar{H_a^N} = e^{-T^{(0)}} H_a^N e^{T^{(0)}}$

$$= H_a^N + \left[H_a^N, T^{(0)}\right] + \frac{1}{2!}\left[\left[H_a^N, T^{(0)}\right]\right] + ...$$

$$= H_a^N + \{\widehat{H_a^N, T^{(0)}}\} + \frac{1}{2!}\{\{\widehat{H_a^N, T^{(0)}}\} T^{(0)}\} + ...$$

This gives,

$$\langle \Phi_a^{r\prime}| \widehat{H_a^N T_1^{(1)}} + \widehat{H_a^N T_2^{(1)}} + \{\widehat{H_a^N T_1^{(0)}} T_1^{(1)} + \{\widehat{H_a^N T_1^{(0)}} T_2^{(1)}\} + \{\widehat{H_a^N T_2^{(0)}} T_1^{(1)}\} \tag{6.0.2}$$

$$+\{\widehat{H_a^N T_2^{(0)}} T_2^{(1)}\} + \frac{1}{2!}\{\widehat{H_a^N T_1^{(0)} T_1^{(0)}} T_1^{(1)}\}|\Phi_0\rangle = -\langle \Phi_a^{r\prime}|H_{EDM} + \widehat{H_{EDM} T_1^{(0)}}$$

$$+\widehat{H_{EDM} T_2^{(0)}} + \frac{1}{2!}\{\widehat{H_{EDM} T_1^{(0)} T_1^{(0)}}\}|\Phi_0\rangle$$

This equation is same as that obtained with different approach. Similarly, the doubles equation is given by

$$\langle \Phi_{ab}^{rs}|\{\widehat{H_a^N T_1^{(1)}}\} + \{\widehat{H_a^N T_2^{(1)}}\} + \frac{1}{2!}\left[\widehat{H_a^N T_1^{(0)} T_1^{(1)}} + 2\widehat{H_a^N T_1^{(0)} T_2^{(1)}} + \widehat{H_a^N T_2^{(0)} T_2^{(1)}} + \widehat{H_a^N T_2^{(0)} T_1^{(1)}}\right] + \tag{6.0.3}$$

$$\frac{1}{3!}\left[\widehat{H_a^N T_1^{(0)} T_1^{(0)} T_1^{(1)}} + 3\widehat{H_a^N T_1^{(0)} T_1^{(0)} T_2^{(1)}} + 3\widehat{H_a^N T_1^{(0)} T_2^{(0)} T_1^{(1)}}\right] +$$

$$\frac{1}{4!}\left[\widehat{H_a^N T_1^{(0)} T_1^{(0)} T_1^{(0)} T_1^{(0)}}\right]\}|\Phi_0\rangle = -\langle \Phi_{ab}^{rs}|\widehat{H_{EDM} T_2^{(0)}} + \widehat{H_{EDM} T_1^{(0)} T_2^{(0)}}|\Phi_0\rangle$$

Note that these equations for the unperturbed CC equations mean that the contributions,

$$\langle \Phi_a^r|\bar{H}_a^N|\Phi_0\rangle = 0$$

$$\langle \Phi_{ab}^{rs}|\bar{H}_a^N|\Phi_0\rangle = 0.$$

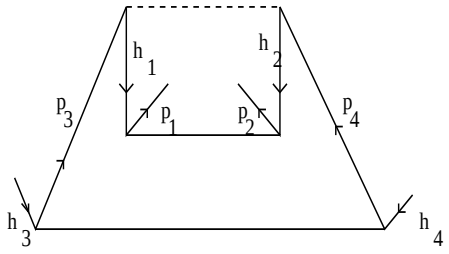

Figure 6.0.1: Diagram representing $V_N T_2^{(0)} T_2^{(0)}$

Computationally , these equations can be written in a more efficient way, by defining barred operators. We define $\bar{H}_a^N = e^{-T^{(0)}} H_a^N e^{T^{(0)}}$. This definition enables one to decrease the computational time which is illustrated below. Consider Fig.6.0.1.

Without the barred operator, the total no. of operations is $N_{nobar} = n_p^4 \times n_h^4$ where n_p and n_h re the no. of particle and hole orbitals respectively. If a barred operator is used, the no. of operations will be

- To compute the barred part, $N_{bar} = n_p^4 \times n_h^2$ (four particle and two hole orbitals).
- When inserting the barred two-electron part in T_1 equations, $N = n_p^4 \times n_h^2$. Therefore, $N_{total} = 2 \times n_p^4 \times n_h^2$.

Taking the ratio,

$$\frac{N_{nobar}}{N_{total}} = \frac{n_p^4 \times n_h^4}{2 \times n_p^4 \times n_h^2} = \frac{n_h^2}{2}.$$

Which imples,

$$N_{nobar} = \frac{n_h^2}{2} \times N_{total}$$

For $n_h = 20$,

$$N_{nobar} = \frac{20 \times 20}{2} \times N_{total}$$

$$\approx 200 \times N_{total}$$

This is for one iteration. For each iteration, N_{nobar} is multiplied by the no. of iterations. Due to this reason the operator $\bar{H}_a^N$ is written in terms of $\bar{H}_a^N = \bar{f}_a^N + \bar{V}_a^N$ and is computed first and then is contracted with $T^{(1)}$. Consider the H_{EDM} perturbed Coupled-cluster equations Eq.5.0.2,

$$\left[\bar{H}_0^N, T^{(1)}\right] |\Phi_0\rangle = -\bar{H}_{EDM} |\Phi_0\rangle \tag{6.0.4}$$

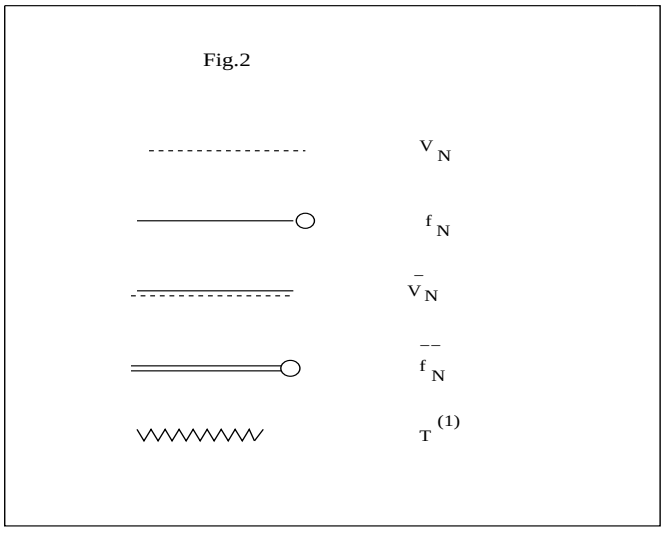

Figure 6.0.2: Notation for interaction lines

Projecting with singly and doubly excited determinants to get the equations for CC singles and doubles respectively,

$$\langle \Phi_a^r | \left[\bar{H}_0^N, T^{(1)} \right] | \Phi_0 \rangle = -\langle \Phi_a^r | \bar{H}_{EDM} | \Phi_0 \rangle \quad (6.0.5)$$

$$\langle \Phi_{ab}^{rs} | \left[\bar{H}_0^N, T^{(1)} \right] | \Phi_0 \rangle = -\langle \Phi_{ab}^{rs} | \bar{H}_{EDM} | \Phi_0 \rangle \quad (6.0.6)$$

This gives

$$\langle \Phi_a^r | \{ \widehat{\bar{H}_0^N, T^{(1)}} \} | \Phi_0 \rangle = -\langle \Phi_a^r | \bar{H}_{EDM} | \Phi_0 \rangle$$

and

$$\langle \Phi_{ab}^{rs} | \{ \widehat{\bar{H}_0^N, T^{(1)}} \} | \Phi_0 \rangle = -\langle \Phi_{ab}^{rs} | \bar{H}_{EDM} | \Phi_0 \rangle$$

Substituting $T^{(1)} = T_1^{(1)} + T_2^{(1)}$, and $\bar{H}_a^N = \bar{f}_N + \bar{V}_N$,

$$\langle \Phi_a^r | \{ \widehat{f_N T_1^{(1)}} + \widehat{f_N T_2^{(1)}} + \widehat{V_N T_1^{(1)}} + \widehat{V_N T_2^{(1)}} \} | \Phi_0 \rangle = -\langle \Phi_a^r | \bar{H}_{EDM} | \Phi_0 \rangle$$

and

$$\langle \Phi_{ab}^{rs} | \{ \widehat{f_N T_1^{(1)}} + \widehat{f_N T_2^{(1)}} + \widehat{V_N T_1^{(1)}} + \widehat{V_N T_2^{(1)}} \} | \Phi_0 \rangle = -\langle \Phi_{ab}^{rs} | \bar{H}_{EDM} | \Phi_0 \rangle$$

Consider the equation for singles. Fig.6.0.2 shows the notation used.The diagrams for the barred operators, $\bar{f}_N T^{(1)}$ and $\bar{V}_N T^{(1)}$ for singles are shown in the Fig.6.0.3 and doubles in Fig.6.0.4. The diagrams for $\bar{f}_N$ and $\bar{V}_N$ for singles and doubles should be as shown in Fig.6.0.5 and Fig.6.0.6 respectively.

Fig.3a

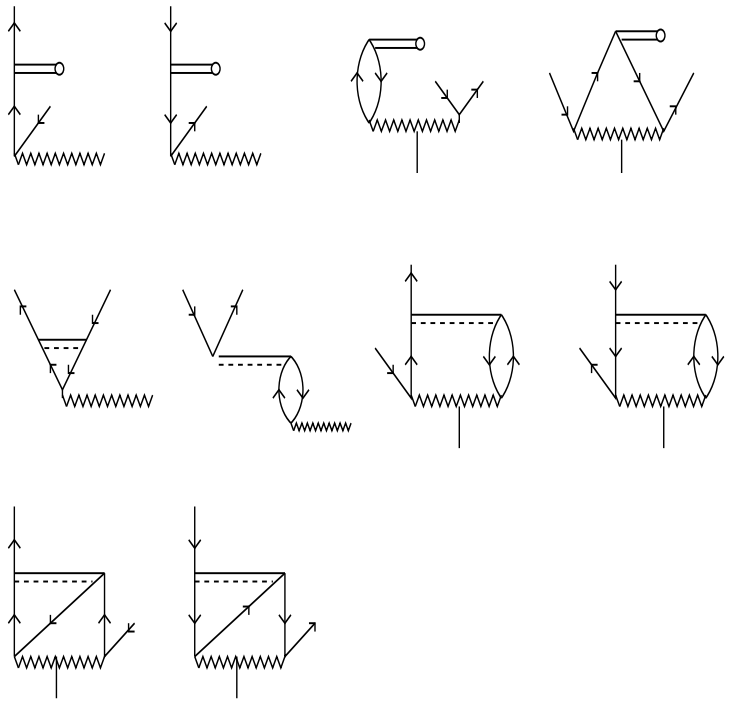

Figure 6.0.3: Contribution of $\bar{f}_N T^{(1)}$ and $\bar{V}_N T^{(1)}$ to singles

Fig.3b

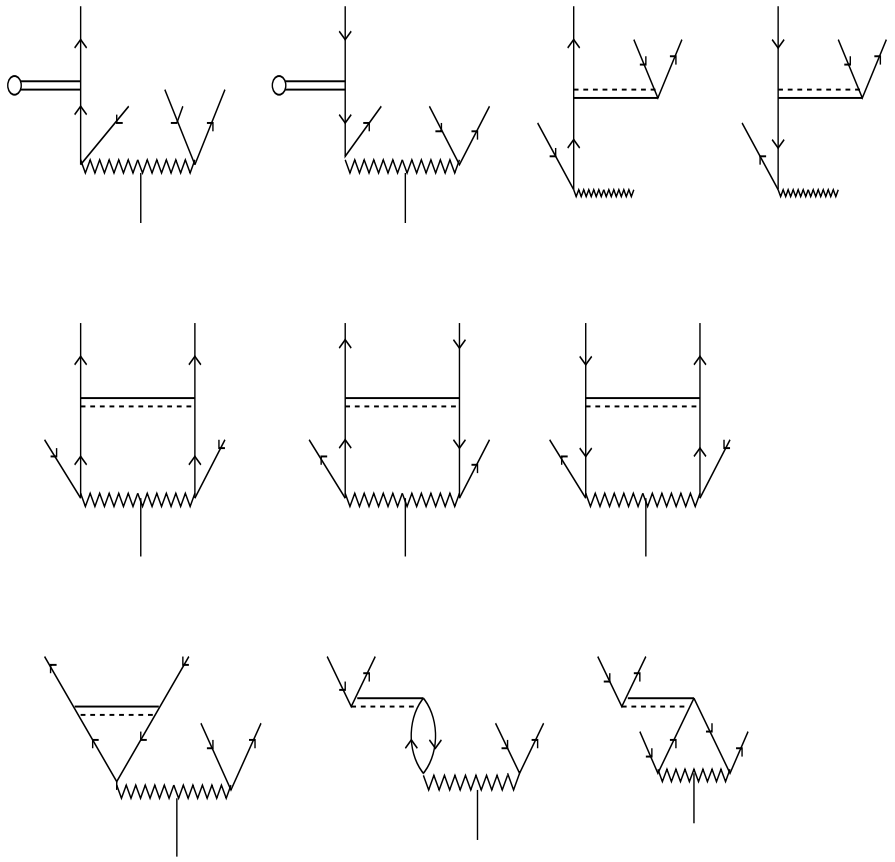

Figure 6.0.4: Contribution of $\bar{f}_N T^{(1)}$ and $\bar{V}_N T^{(1)}$ to doubles

Fig.4a

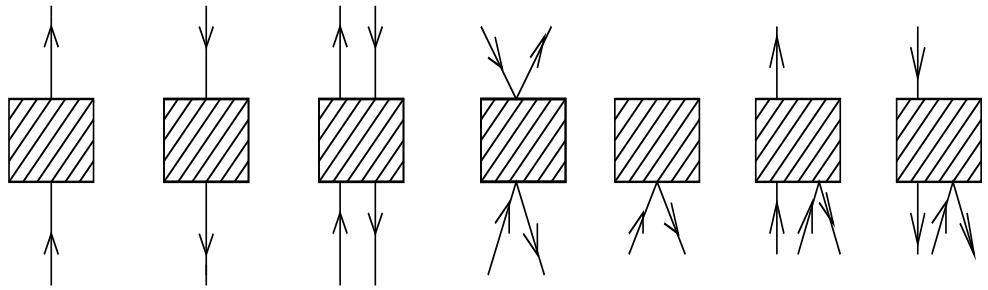

Figure 6.0.5: Contribution of $\bar{f}_N$ and $\bar{V}_N$ to singles

Fig.4b

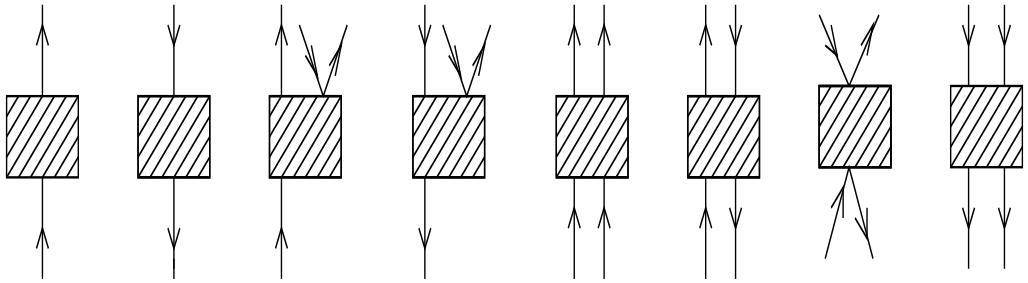

Figure 6.0.6: Contribution of $\bar{f}_N$ and $\bar{V}_N$ to doubles

7 Connection between CI, MBPT and CCT.

The exact atomic wave function in Coupled-cluster theory is expressed as

$$|\Psi_{CC}\rangle = \Omega|\Phi_0\rangle = e^T|\Phi_0\rangle$$

where Ω is the wave operator, $|\Phi_0\rangle$ is the reference state and T is the hole-particle excitation operator. In the present discussion $T = T_1 = \sum_{a,p} a_p^\dagger a_a t_a^p$. This gives

$$|\Psi_{CC}\rangle = \left[1 + T_1 + \frac{T_1^2}{2!} + ...\right]|\Phi_0\rangle \tag{7.0.1}$$

and

$$T_1|\Phi_0\rangle = \sum_{a,p} a_p^\dagger a_a|\Phi_0\rangle.t_a^p = |\Phi_a^p\rangle t_a^p$$

t_a^p is the probability amplitude for the excitation from 'a' to 'p'. Consider the CI wavefunction,

$$|\Psi_{CI}\rangle = C_0|\Phi_0\rangle + \sum_s C_s|\Phi_s\rangle + C_d \sum_d |\Phi_d\rangle + ... \tag{7.0.2}$$

where $|\Phi_0\rangle$, $|\Phi_s\rangle$, $|\Phi_d\rangle$ ... form a complete set of basis vectors in Hilbert space. Comparing Eq.7.0.1 and Eq.7.0.2,

$$T_1|\Phi_0\rangle = \sum_{a,p} |\Phi_a^p\rangle t_a^p = \sum_s C_s|\Phi_s\rangle$$

Hence, T_1 is equivalent to the set of all the single excitations as given by the CI wavefunction. From Eq.7.0.1 and Eq.7.0.2 it can also be noted that to get quadruple excitations, it is necessary to include the quadruple excitations explicitly in the CI wavefunction, but the CC wavefunction can give quadruple excitations through T_1^2 term at a lower level of truncation of the exponential. The $|\Phi_s\rangle$ of the CI is identical to $|\Phi_a^p\rangle$ of CCT. T_1 case is simpler. But to establish the equivalence between CCT and CI for T_2, it is required to consider the contribution to T_2 arising from T_1^2 also. Consider the MBPT wavefunction in terms of the unperturbed state,

$$|\Psi\rangle = |\Phi_0\rangle + |\Phi_0^1\rangle + |\Phi_0^2\rangle + ... \tag{7.0.3}$$

where $|\Phi_0\rangle$ is the unperturbed wavefunction and others are the higher order corrections to $|\Phi_0\rangle$.

$$|\Phi_0^1\rangle = \sum_{I\neq 0} |\Phi_I\rangle \frac{\langle\Phi_I|H'|\Phi_0\rangle}{E_0 - E_I}$$

$|\Phi_0^1\rangle$ can be expanded in terms of the complete set,

$$|\Phi_0^1\rangle = \sum_s C_s^1|\Phi_s\rangle + \sum_d C_d^1|\Phi_d\rangle + ...$$

Similarly,

$$|\Phi_0^2\rangle = \sum_s C_s^2|\Phi_s\rangle + \sum_d C_d^2|\Phi_d\rangle + ...$$

where for $|\Phi_0^1\rangle$, 'I' stands for all the single excited intermediate states. The exact wavefunction $|\Psi\rangle$ can now be written as

$$|\Psi\rangle = |\Phi_0\rangle + \sum_s \left[C_s^1 + C_s^2 + ...\right]|\Phi_s\rangle + \sum_d \left[C_d^1 + C_d^2 + ...\right]|\Phi_d\rangle + ... \tag{7.0.4}$$

$|\Phi_0^1\rangle$ has one order residual coulomb interaction(perturbation), $|\Phi_0^2\rangle$ has two orders, and so on. This implies that there are infinite no. of residual coulomb interactions giving rise to a single excitation, infinite Couplomb interactions giving rise to double excitations and so on, where C_s^1, C_s^2 etc represent 1 order in Coulomb with 1 intermediate state(I), 2 orders in Coulomb with 2

Fig.1

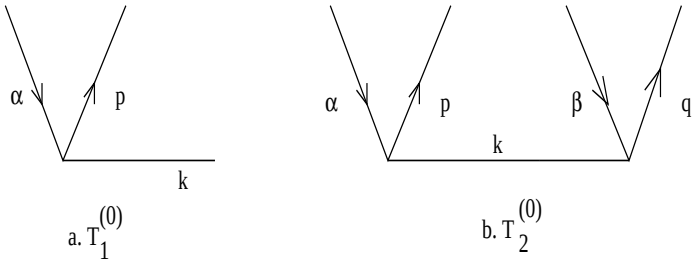

Figure 7.0.1: Unperturbed cluster operators

intermediate states (I,J) respectively. Comparing Eq.7.0.1 and Eq.7.0.4, we get

$$T_1|\Phi_0\rangle = \sum_s \left[C_s^1 + C_s^2 + ...\right] |\Phi_s\rangle \tag{7.0.5}$$

which indicates that T_1 contains infinite orders of Coulomb interaction corresponding to all possible single excitations. The above T_1 refers to the unperturbed cluster operator $T_1^{(0)}$. The H_{EDM} perturbed operator $T_1^{(1)}$ contains, in addition to infinite orders in Coulomb perturbation, one order in H_{EDM}. The rank of the H_{EDM} decides the j-value of the orbitals 'a' and 'p'' where prime indicates that 'p' and 'p'' are opposite in parity. The Fig.7.0.1 below shows the operators $T_1^{(0)}$ and $T_1^{(1)}$ respectively.

8 Selection rules of H_{EDM} perturbed cluster amplitudes :

To derive the selection rules associated with the H_{EDM} perturbed cluster amplitudes, it is appropriate to highlight the nature of the interaction Hamiltonians involved. The electric-dipole moment(EDM) of an atom can arise from various sources :

1. EDM of an electron d_e.
2. P,T-odd electron-nucleon interactions which could be 'scalar' (scalar-pseudoscalar),'tensor'(tensor-pseudotensor) or 'pseudo-scalar' (pseudoscalar-scalar) couplings.
3. P,T-odd electron-electron couplings(is negligible in contribution due to the strength of the interaction).

Consider the atomic EDM arising from P,T-odd electron-nucleon interactions and treat the nucleus non-relativistically. The P,T-odd scalar-pseudoscalar kind of interaction leads to an interaction Hamiltonian of the type,

$$H_{e-N}^{EDM,S} = \frac{iG_F C_S}{\sqrt{2}} \sum_i (\beta_i \gamma_{5i}) \rho_N(r) \tag{8.0.1}$$

where, G_F is the Fermi's coupling constant, C_S represents scalar coupling constant, $\rho_N(r)$ is the nuclear density and β and γ_5 represent Dirac matrices. Similarly the tensor-pseudotensor electron-nucleus interaction Hamiltonian has the form,

$$H_{e-N}^{EDM,T} = \frac{iG_F C_T}{\sqrt{2}} \sum_i \boldsymbol{\sigma_i} \cdot \boldsymbol{\gamma_i} \rho_N(r) \tag{8.0.2}$$

The operator in the electron space is a vector of rank 1. C_T represents the tensor coupling constant. Hence in the case of a scalar and a tensor interaction, it is important how the rank of the interaction Hamiltonian in the electron space is incorporated into the perturbed cluster amplitudes. Consider the diagrammatic representation of $T_1^{(1)}$ shown in Fig.8.0.1 . In terms of the multipole components

$$T_1{}^{(1)} = \sum_q (T_1{}^{(1)})_q^1 \tag{8.0.3}$$

Algebraically, $T_1^{(1)}$ can be written as

$$T_1^{(1)} = \sum_{a,p} a_p^\dagger a_a t_a^p \tag{8.0.4}$$

where, p is a particle, hence represented by an out-going line, and a is a hole represented by an incoming line, and t_a^p is the corresponding cluster amplitude.

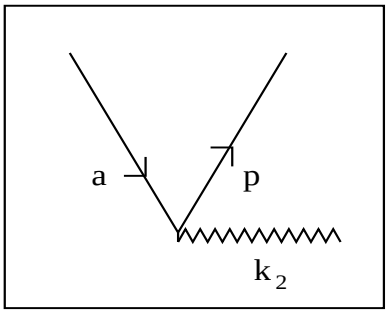

Figure 8.0.1: Diagram representing $T_1^{(1)}$

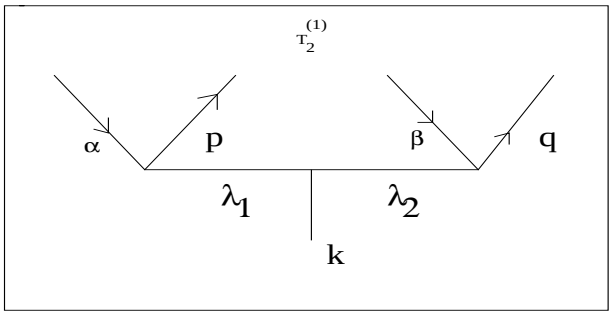

Figure 8.0.2: Diagram representing $T_2^{(1)}$

The rank of $T_1^{(1)}$ is $k_2 = 1$. The vertex in the $T_1^{(1)}$ diagram, should satisfy the triangular condition

$$|J_a - 1| \leq J_p \leq J_a + 1,$$

and the magnetic moment conservation

$$m_a + m_p + q = 0,$$

The parity of the orbitals a and p are opposite therefore,

$$(-1)^{l_a + l_p} = -1.$$

Consider fig.6 representing $\{\widehat{H_{EDM}T_2^{(0)}}\}$. l denotes λ, k_1 and k_2 represent the ranks of H_{EDM} and $T_2^{(0)}$ repectively. λ arises due to the coupling of the angular momentum vectors J_p and J_a. This diagram can be reduced to a product of an open diagram, an angular factor and a 3J-symbol using angular momentum algebra. Since $k_1 = 1$

$$(-1)^{l_p + l_q} = \text{odd}. \tag{8.0.5}$$

The three vertices in the open part satisfy the triangular condition

$$|J_a - J_p| \leq \lambda \leq J_a + J_p$$

$$|J_b - J_r| \leq k_2 \leq J_b + J_r$$

$$|\lambda - k_2| \leq k_1 \leq |\lambda + k_2|$$

Using Eq.8.0.5 and

$$(-1)^{l_q + l_a}(-1)^{l_b + l_r} = even$$

we get

$$(-1)^{l_a + l_p} = -(-1)^{l_b + l_r}.$$

The open part of the diagram has an additional line k_1 representing the vector nature of the $T_2^{(1)}$ operator. This open part gives an idea as to where in the diagram this line can be implemented. The factor in the diagram is,

$$\sum_{\lambda} [\lambda] \, (-1)^{J_a + J_p + \lambda}(-1)^{k_1 + k_2 + \lambda}.$$

Fig 7. shows $\{\widehat{H_N T_1^{(1)}}\}$ contributing to $T_2^{(1)}$. This diagram can be reduced to an open part representing $T_2^{(1)}$ times an angular factor. l_1 represents λ_1. a and b are holes and p, q and r are particles. Triangular conditions at the three vertices(shown in circles) are given by

$$|J_a - J_p| \leq \lambda_1 \leq J_a + J_p$$

$$|J_r - J_b| \leq k_1 \leq J_r + J_b$$

$$|\lambda_1 - k_1| \leq k_2 \leq \lambda_1 + k_1.$$

Since k_1 is a Coulomb line, vertex 3 satisfies

$$(-1)^{l_b + l_r + k_1} = even.$$

and $k_2 = 1$ gives the condition

$$(-1)^{l_a + l_p + k_1} = -(-1)^{l_b + l_r + k_1}$$

For $T_2^{(1)}$ to be even in parity, either both the vertices 1 and 2 have to be even in parity or have to be odd. Consider the two case separately.

1. If the vertices 1 and 2 are even in parity, then

$$(-1)^{l_a + l_p + \lambda_1} = even;$$

$$(-1)^{k_1 + \lambda_1 + 1} = even.$$

which gives $\lambda_1 + k_1$ =odd. Hence $\lambda_1 \neq k_1$ and $|k_1 - 1| \leq \lambda_1 \leq k_1 + 1$ as k_2 =1.

2. If the vertices 1 and 2 are odd in parity, then

$$(-1)^{l_a + l_p + \lambda_1} = odd;$$

$$(-1)^{k_1 + \lambda_1 + 1} = odd.$$

Using

$$|\lambda_1 - k_1| \leq k_2 \leq \lambda_1 + k_1$$

gives $\lambda_1 = k_1$.

The angular factor in the diagram is given by

$$\sum_{\lambda_1} [\lambda_1](-1)^{2J_a}$$

It is important to note that there is a $\sum_{\lambda_1}$. Hence, if there is no restriction imposed on the vertices 1 and 2 in the figure, this diagram has to be summed over all λ_1. On the other hand, if the vertices 1 and 3 are considered to be opposite in parity, then the vertex 2 should be odd in parity. This gives

$$(-1)^{k_1 + \lambda_1 + 1} = odd.$$

which leads to $\lambda_1 = k_1$. But this condition for the vertices 1 and 3 is not general and hence is not imposed.

9 The tensor-pseudotensor H_{EDM} matrix element

Consider the general matrix element of H_{EDM} between $|\Phi_a\rangle$ and $|\Phi_b\rangle$, $\langle\Phi_a|H_{EDM}|\Phi_b\rangle$ where H_{EDM} has the form given in Eq.8.0.2. Keeping the constants aside for the moment, consider

$$\langle\Phi_a|H_{EDM}|\Phi_b\rangle = \langle\Phi_a|i\beta\alpha_z I_z \rho_N(r)|\Phi_b\rangle$$

Consider the Z-axis as the axis of quantisation.

$$\langle\Phi_a|H_{EDM}|\Phi_b\rangle = iI_z\langle\Phi_a|i\beta\alpha_z \rho_N(r)|\Phi_b\rangle \tag{9.0.1}$$

The wavefunctions $|\Phi_a\rangle$ and $|\Phi_b\rangle$ can be represented in terms of the two-component Dirac wavefunctions given by,

$$|\Phi_a\rangle = \frac{1}{r}\begin{pmatrix} P_a(r)\chi_{\kappa_a,m_a}(\theta,\phi) \\ iQ_a(r)\chi_{-\kappa_a,m_a}(\theta,\phi) \end{pmatrix}$$

and

$$|\Phi_b\rangle = \frac{1}{r}\begin{pmatrix} P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi) \\ iQ_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi) \end{pmatrix}$$

The Dirac matrices, β and α are given by

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}; \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$$

Substituting for β, α_z in Eq.9.0.1, we get

$$\langle \Phi_a | H_{EDM} | \Phi_b \rangle =$$

$$\int \frac{1}{r^2} \left[\begin{array}{cc} P_a(r)\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi) & -iQ_a(r)\chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi) \end{array} \right] \begin{pmatrix} 0 & \sigma_z \\ -\sigma_z & 0 \end{pmatrix} \left[\begin{array}{c} P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi) \\ iQ_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi) \end{array} \right]$$

$$\times \rho_N(r) r^2 dr d\Omega(iI_z)$$

$$= \int \left[\begin{array}{cc} P_a(r)\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi) & -iQ_a(r)\chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi) \end{array} \right] \left[\begin{array}{c} \sigma_z(i)Q_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi) \\ -\sigma_z(i)P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi) \end{array} \right]$$

$$\rho_N(r) dr d\Omega(iI_z)$$

Simplifying further,
$\langle \Phi_a | H_{EDM} | \Phi_b \rangle =$

$$= \int \left[P_a(r)\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)\sigma_z Q_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi)(i) \right] +$$

$$\left[Q_a(r)\chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi)\sigma_z P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi)(i) \right] \rho_N(r) dr d\Omega(iI_z)$$

Separating the integrals for radial and angular parts,

$$\int P_a(r)Q_b(r)\rho_N(r)dr \underbrace{\int \chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)\sigma_z\chi_{-\kappa_b,m_b}(\theta,\phi)d\Omega}_{I1}(i)(iI_z) \qquad (9.0.2)$$

$$+ \int Q_a(r)P_b(r)\rho_N(r)dr \underbrace{\int \chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi)\sigma_z\chi_{\kappa_b,m_b}(\theta,\phi)d\Omega}_{I2}(i)(iI_z)$$

To calculate the specific angular matrix elements corresponding to $\langle \Phi_{Ks_{1/2}} | H_{EDM} | \Phi_{K'p_{1/2}} \rangle$ and $\langle \Phi_{Ks_{1/2}} | H_{EDM} | \Phi_{K'p_{3/2}} \rangle$ we evaluate the respective angular parts, I1 and I2 in Eq.9.0.2.

Consider the first integral, I1 for $\langle \Phi_{Ks_{1/2}} | H_{EDM} | \Phi_{K'p_{3/2}} \rangle$:

$$I1 = \int \chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)\sigma_z\chi_{-\kappa_b,m_b}(\theta,\phi)d\Omega$$

$\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)$: κ_a = -1 $J_a = 1/2$ This angular wave function is for the upper component of $\Phi_a\rangle$. Hence, $l_a = (J_a + Sign(\kappa_a) \times 1/2) = 0$. =¿$m^l_a = 0$ and $s_a = 1/2$. Choose the projection of the total angular momentumi to be the highest value. $M_a = 1/2 = 0 + 1/2$. The state $|J_a, M_a\rangle = |1/2, 1/2\rangle = |0,0\rangle|1/2,1/2\rangle$ in the L-S basis. Writing $\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)$ in the uncoupled basis,

$$\chi_{\kappa_a,m_a}(\theta,\phi) = \sum_{m^l_a,m^s_a} |l_a, m^l_a\rangle \times |s_a, m^s_a\rangle \langle l_a, m^l_a, s_a, m^s_a | J_a, M_a\rangle$$

$$= |0,0\rangle|\frac{1}{2},\frac{1}{2}\rangle = Y_0^0|\alpha\rangle$$

where $|\alpha\rangle$ represents the wavefunction of a spin-up particle and Y_0^0, the spherical harmonics.
Consider $\chi_{-\kappa_b,m_b}(\theta,\phi)$: This corresponds to the lower component of $|\Phi_b\rangle$. The orbital angular momenta of the upper and lower components l and l' respectively are related as $l' = 2J - l$. We now have, $\kappa_b = -2$ $J_b = 3/2$ The kappa for the lower component, $-\kappa_b = 2$. Therefore, $l'_b = 2J_b - l_b$ and $l_b = 1$. Hence, $l'_b = 2$. From Wigner-Eckart theorem, the multipole moments, M_a, M_b and q satisfy $-M_a + q + M_b = 0$. Hence, $M_a = M_b$. Hence choose $M_b = 1/2$. Therefore,

$$\chi_{-\kappa_b,m_b}(\theta,\phi) = |2,0\rangle|\frac{1}{2},\frac{1}{2}\rangle\langle 2,0;\frac{1}{2},\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle +$$

$$|2,1\rangle|\frac{1}{2},-\frac{1}{2}\rangle\langle 2,1frac12,-\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle$$

$$= Y_2^0|\alpha\rangle\langle 2,0;\frac{1}{2},\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle + Y_2^1|\beta\rangle\langle 2,1;\frac{1}{2},-\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle$$

Now,

$$\sigma_z\chi_{-\kappa_b,m_b}(\theta,\phi) = Y_2^0|\alpha\rangle\langle 2,0;\frac{1}{2},\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle - Y_2^1|\beta\rangle\langle 2,1;\frac{1}{2},-\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle.$$

The integral I1 becomes,

$$I1 = \int \chi^\dagger_{\kappa_a,m_a}(\theta,\phi)\sigma_z\chi_{-\kappa_b,m_b}(\theta,\phi)d\Omega = 0$$

Consider I2:
$\chi_{\kappa_b,m_b}(\theta,\phi)$:
$\kappa_b = -2$, $J_b = 3/2$, l_b=3/2-1/2=1 =¿ m_b^l=-1, 0, 1. Fix $M_b = 1/2$.

$$\chi_{\kappa_b,m_b}(\theta,\phi) = Y_1^0|\alpha\rangle\langle 1,0;\frac{1}{2},\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle + Y_1^1|\beta\rangle\langle 1,1;\frac{1}{2},-\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle$$

$$\sigma_z\chi_{\kappa_b,m_b}(\theta,\phi) = Y_1^0|\alpha\rangle\langle 1,0;\frac{1}{2},\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle - Y_1^1|\beta\rangle\langle 1,1;\frac{1}{2},-\frac{1}{2}|\frac{3}{2},\frac{1}{2}\rangle$$

$\chi_{-\kappa_a,m_a}(\theta,\phi)$:
$\kappa_a = -1$, $-\kappa_a = 1$, $J_a = 1/2$, $l'_a = 2J_a - l_a = 1$. Hence, $m_a^l = -1, 0, 1$. Fix $M_a = \frac{1}{2}$.

$$\chi_{-\kappa_a,m_a}(\theta,\phi) = Y_1^0|\alpha\rangle\langle 1,0;\frac{1}{2},\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle + Y_1^1|\beta\rangle\langle 1,1;\frac{1}{2},-\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle$$

Using the orthogonality property(??) of the Spherical tensors Y_l^m and Clebsch-Gordan coefficients, we get I2=$-\frac{2}{3}\sqrt{2}$. The EDM matrix element,

$$\langle\Phi_{Ks_{1/2}}|H_{EDM}|\Phi_{K'p_{3/2}}\rangle = (i^2)(I_z)\left(-\frac{2}{3}\sqrt{2}\right)\int Q_a(r)P_b(r)\rho_N(r)dr \qquad (9.0.3)$$

10 Calculation of the H_{PTV} matrix elements

The effective atomic Hamiltonian whose EDM is induced by electron EDM is given by,

$$H_{eff} = \sum_e 2icd_e\beta\gamma_5 p^2 \tag{10.0.1}$$

$$\beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}; \gamma_5 = \begin{bmatrix} 0 & -I \\ -I & 0 \end{bmatrix}$$

Hence,

$$H_{eff} = \sum_e 2icd_e \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} 0 & -I \\ -I & 0 \end{bmatrix} p^2$$

where

$$p^2 = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{L^2}{r^2} \tag{10.0.2}$$

The matrix element of H_{eff} between two orbitals $|\Psi_i\rangle$ and $\Psi_j\rangle$ is

$$\langle\Psi_i|H_{eff}|\Psi_j\rangle = 2icd_e \int d^3r \frac{1}{r} \begin{pmatrix} P_i(r)\chi^\dagger_{\kappa_i m_i} & -iQ_i(r)\chi^\dagger_{-\kappa_i m_i} \end{pmatrix} \begin{bmatrix} 0 & -p^2 \\ p^2 & 0 \end{bmatrix} \frac{1}{r} \begin{pmatrix} P_j(r)\chi_{\kappa_j m_j} \\ iQ_j(r)\chi_{-\kappa_j m_j} \end{pmatrix}$$

$$= 2icd_e \int d^3r \frac{1}{r} \begin{pmatrix} P_i(r)\chi^\dagger_{\kappa_i m_i} & -iQ_i(r)\chi^\dagger_{-\kappa_i m_i} \end{pmatrix} \cdot \frac{1}{r} \begin{pmatrix} -p^2 iQ_j(r)\chi_{-\kappa_j m_j} \\ p^2 P_j(r)\chi_{\kappa_j m_j} \end{pmatrix} \tag{10.0.3}$$

$$= 2icd_e \int d^3r \frac{1}{r} \left[\underbrace{P_i(r)\chi^\dagger_{\kappa_i m_i}(-p^2)\frac{(i)}{r}Q_j(r)\chi_{-\kappa_j m_j}}_{I_1} - \underbrace{iQ_i(r)\chi^\dagger_{-\kappa_i m_i}(p^2)\frac{1}{r}P_j(r)\chi_{\kappa_j m_j}}_{I_2} \right] \tag{10.0.4}$$

Consider

$$I_1 = \int d^3r \frac{1}{r} P_i(r)\chi^\dagger_{\kappa_i m_i}(-p^2)\frac{(i)}{r}Q_j(r)\chi_{-\kappa_j m_j}$$

$$p^2 = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{r^2}$$

$$p^2\left[\frac{1}{r}Q_j(r)\chi_{-\kappa_j m_j}\right] = \left[-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\frac{1}{r}Q_j(r) + \frac{l'_j(l'_j+1)}{r^2}\frac{Q_j(r)}{r}\right]\chi_{-\kappa_j m_j}$$

where l'_j denotes the orbital angular momentum of the small component of $|\Psi_j\rangle$.

$$= \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(-Q_j(r) + r\frac{\partial Q_j(r)}{\partial r}\right) + \frac{l'_j(l'_j+1)}{r^2}\frac{Q_j(r)}{r}\right]\chi_{-\kappa_j m_j}$$

$$= \left[-\frac{1}{r^2}\left(-\frac{\partial Q_j(r)}{\partial r} + \frac{\partial Q_j(r)}{\partial r} + r\frac{\partial^2 Q_j(r)}{\partial r^2}\right) + \frac{l'_j(l'_j+1)}{r^2}\frac{Q_j(r)}{r}\right]\chi_{-\kappa_j m_j}$$

$$= \left[-\frac{1}{r} Q_j(r)'' + \frac{l'_j(l'_j+1)}{r^2} \frac{Q_j(r)}{r} \right] \chi_{-\kappa_j m_j}$$

Hence,

$$I_1 = \int d^3r \frac{1}{r} P_i(r) \chi^\dagger_{\kappa_i m_i}(-i) \left[-\frac{1}{r} Q_j(r)'' + \frac{l'_j(l'_j+1)}{r^2} \frac{Q_j(r)}{r} \right] \chi_{-\kappa_j m_j}$$

$$= \int dr P_i(r) Q_j(r)'' \chi^\dagger_{\kappa_i m_i} \chi_{-\kappa_j m_j}(i) d\Omega + \int dr P_i(r) Q_j(r) \chi^\dagger_{\kappa_i m_i} \frac{l'_j(l'_j+1)}{r^2} \chi_{-\kappa_j m_j}(i) d\Omega$$

The angular integrals satisfy the orthogonality condition,

$$\int \chi^\dagger_{\kappa_a m_a} \chi_{-\kappa_b m_b} d\Omega = \delta(\kappa_a, -\kappa_b)\, \delta(m_a, m_b) \tag{10.0.5}$$

$$I_1 = \int dr P_i(r) Q_j(r)''(i) \delta(\kappa_i, -\kappa_j)\, \delta(m_i, m_j) +$$

$$\int dr P_i(r) Q_j(r) \frac{l'_j(l'_j+1)}{r^2}(i) \delta(\kappa_i, -\kappa_j)\, \delta(m_i, m_j)$$

$$= \int dr \left[P_i(r) Q_j(r)''(i) + P_i(r) Q_j(r) \frac{l'_j(l'_j+1)}{r^2}(i) \right] \delta(\kappa_i, -\kappa_j)\, \delta(m_i, m_j) \tag{10.0.6}$$

For the large component, $l = j - \frac{1}{2}$ where $\kappa < 0$ and $l = j + \frac{1}{2}$ where $\kappa > 0$. For the small component, $l' = 2j - l = 2j - j - \mathrm{Sign}(\kappa)\frac{1}{2} = j - \mathrm{Sign}(\kappa)\frac{1}{2}$.

Consider integral I_2.

$$I_2 = \int d^3r \frac{1}{r} \left[i Q_i(r) \chi^\dagger_{-\kappa_i m_i}(p^2) \frac{1}{r} P_j(r) \chi_{\kappa_j m_j} \right]$$

$$= \int d^3r \frac{1}{r}(i) Q_i(r) \chi^\dagger_{-\kappa_i m_i} \left[-\frac{P_j(r)''}{r} + \frac{l_j(l_j+1)}{r^2} \frac{P_j(r)}{r} \chi_{\kappa_j m_j} \right]$$

$$= \int dr \left[-Q_i(r) P_j(r)'' + \frac{l_j(l_j+1)}{r^2} Q_i(r) P_j(r) \right] \delta(-\kappa_i, \kappa_j)\, (i) \delta(m_i, m_j)$$

Substituting I_1 and I_2 in Eqn.10.0.4,

$\langle \Psi_i | H_{eff} | \Psi_j \rangle =$

$$= 2icd_e \int dr(i) \left[P_i(r) Q''_j - P_i(r) Q_j(r) . \frac{l'_j(l'_j+1)}{r^2} \right] \delta(\kappa_i, -\kappa_j)\, \delta(m_i, m_j) +$$

$$2icd_e(i) \int dr \left[Q_i P''_j - \frac{l_j(l_j+1)}{r^2} Q_i(r) P_j(r) \right] \delta(-\kappa_i, \kappa_j)\, \delta(m_i, m_j)$$

$$= 2cd_e \int dr \left[-P_i(r) Q''_j(r) + P_i(r) Q_j(r) \frac{l'_j(l'_j+1)}{r^2} \right] \delta(\kappa_i, -\kappa_j)\, \delta(m_i, m_j)$$

$$+2cd_e \int dr \left[-Q_i P''_j(r) + \frac{l_j(l_j+1)}{r^2} Q_i(r) P_j(r) \right] \delta(-\kappa_i, \kappa_j)\, \delta(m_i, m_j) \}$$