

Coupled Clusters Response Properties

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1 CC equations

The CC energy is given by

$$E_{CC} = \langle \text{HF} | e^{-T} H e^T | \text{HF} \rangle. \quad (1)$$

The CC equations (in the linked formulation¹) are given by

$$\langle \mu | e^{-T} H e^T | 0 \rangle = 0 \quad (2)$$

The CC vector is given by

$$|\text{CC}\rangle = e^T |\text{HF}\rangle. \quad (3)$$

The cluster operator for an N -electron system is given by

$$T = T_1 + T_2 + \dots + T_N, \quad (4)$$

$$T_1 = \sum_{ai} \sum_{\sigma_1 \sigma_2} t_{a\sigma_1 i \sigma_2} a_{a\sigma_1}^\dagger a_{i\sigma_2}, \quad (5)$$

$$T_2 = \sum_{abji} \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} t_{a\sigma_1 b \sigma_2 j \sigma_3 i \sigma_4} a_{a\sigma_1}^\dagger a_{b\sigma_2}^\dagger a_{j\sigma_3} a_{i\sigma_4}. \quad (6)$$

The chemistry convention specifies that the indices i, j, k, l index the occupied orbitals, while the indices a, b, c, d index the virtual orbitals. Occupied orbitals are the ones that form the reference state $|\text{HF}\rangle$ while virtual orbitals are the reminder. In a shorthand notation, the products of creation and annihilations operators are replaced with a corresponding excitation operator τ

$$T = t\tau = \sum_{\nu} t_{\nu} \tau_{\nu}. \quad (7)$$

The index of the excitation operator goes over single excitations, double excitations, and so on.

Koch and Jørgensen² also define the excited bras

$$\langle \nu | = \langle \text{HF} | \tau_{\nu}^\dagger, \quad (8)$$

and the excited bras with an extra exponential

$$\langle \bar{\nu} | = \langle \nu | e^{-T} = \langle \text{HF} | \tau_{\nu}^\dagger e^{-T}. \quad (9)$$

2 Lambda equations

The dual of the CC vector, $\langle \text{CC} |$, is no good for calculation of properties, because it breaks the Hellman-Feynman theorem.¹ To fix this issue, the CC theory founders have created an alternative dual vector to $|\text{CC}\rangle$, which assures the Hellman-Feynman theorem is satisfied and the properties make sense. The dual vector is typically called lambda, $\langle \Lambda |$.

The lambda is defined as

$$\langle \Lambda | = \langle \text{HF} | + \sum_{\nu} \zeta_{\nu} \langle \nu | e^{-T} = \left(\langle \text{HF} | + \sum_{\nu} \zeta_{\nu} \langle \nu | \right) e^{-T} \quad (10)$$

The ζ_{ν} coefficients are determined by making sure that the $\langle \Lambda |$ satisfies the Schrödinger equation

$$\langle \Lambda | H = \langle \Lambda | E_{CC}. \quad (11)$$

To find the equations for ζ_{ν} , first the equation Eq. (11) is hit with the cluster operator from the right

$$\langle \Lambda | H e^T = \langle \Lambda | e^T E_{CC}, \quad (12)$$

then it is projected onto the reference determinant, $|\text{HF}\rangle$, and enough many excited determinants, $|\mu\rangle$. Projection onto $|\text{HF}\rangle$ results in an equation that vanishes, for the E_{CC} and T satisfying the CC equations. Projections onto the excited determinants lead to

$$\langle \Lambda | H e^T |\mu\rangle = E_{CC} \langle \Lambda | e^T |\mu\rangle. \quad (13)$$

The rhs simplifies to $E_{CC}\zeta_{\mu}$, leading to the lambda residual equations

$$\langle \Lambda | H e^T |\mu\rangle - E_{CC}\zeta_{\mu} = 0. \quad (14)$$

3 Linear Response Properties

The linear response properties describe the response of a molecule to an external field. This statement is formalized by writing down the system Hamiltonian as

$$H_{sys} = H + V \quad (15)$$

I follow the method of Koch and Jørgensen.² Much of the notation from this work is explained in detail in an earlier work of Olsen and Jørgensen³, as well as in the book by Zubarev.⁴

The coupled cluster linear response function is given by Eq. (94) from Ref. [2]

$$\langle\langle A; B \rangle\rangle_{\omega_1} = \sum_{\mu} \langle \Lambda | [A, \tau_{\mu}] | CC \rangle X_{\mu}^B(\omega_1) + \sum_{\mu} \left(\langle \Lambda | [B, \tau_{\mu}] | CC \rangle + \sum_{\gamma} F_{\mu\gamma} X_{\gamma}^B(\omega_1) \right) X_{\mu}^A(-\omega_1) \quad (16)$$

The matrices $X_\mu^x(\omega)$ are the t amplitudes responses defined in Eq. (95) and (58) or Ref. [2].

$$X_\mu^x(\omega) = \sum_\nu (-\mathbf{A} + \omega \mathbf{I})_{\mu\nu}^{-1} x_\nu, \quad (17)$$

where the x_ν matrix is related to the external perturbation operator, x (e.g., for the electric dipole perturbation this operator is the electric dipole operator $x = \hat{\mu}$, see Ref. [3])

$$x_\nu = \langle \nu | e^{-T} x e^T | \text{HF} \rangle, \quad (18)$$

and the matrix \mathbf{A} is the CC Jacobian

$$A_{\mu\nu} = \langle \mu | e^{-T} [H, \tau_\nu] e^T | \text{HF} \rangle \quad (19)$$

Finally, the $F_{\mu\nu}$ matrix originates from the ζ amplitudes response and is given by Eq. (77) from Ref. [2]

$$F_{\mu\gamma} = \langle \Lambda | [[H, \tau_\mu], \tau_\gamma] | \text{CC} \rangle. \quad (20)$$

One more term from the Eq. (16) has a shortcut notation (following Eq. (76) from Ref. [2])

$$\eta_\nu^x(\omega) = \langle \Lambda | [x^\omega, \tau_\nu] | \text{CC} \rangle, \quad (21)$$

where x^ω is a Fourier transform component of the external field operator. Using this shortcut the Eq. (16) becomes

$$\langle \langle A; B \rangle \rangle_{\omega_1} = \sum_\mu \eta_\mu^A X_\mu^B(\omega_1) + \sum_\mu \left(\eta_\mu^B + \sum_\gamma F_{\mu\gamma} X_\gamma^B(\omega_1) \right) X_\mu^A(-\omega_1). \quad (22)$$

References

- ¹T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular electronic-structure theory* (Wiley, Chichester ; New York, 2000), 908 pp.
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- ⁴D. N. Zubarev, *Nonequilibrium statistical thermodynamics*, Studies in Soviet science (Consultants Bureau, New York, 1974), 489 pp.