A Cluster Expansion Formalism for Direct Calculation of Ionisation Potential and Excitation Energy of Many Electron Systems Using H-F Ground State as Vacuum

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In this note, the authors' recently developed non-perturbative open-shell theory is adapted for direct calculation of ionisation potential and excitation energy of many-electron systems. The H-F ground state is used as the "vacuum" or "core" in order to achieve a transparent separation of the ground state energy. An application to a simple 4π-electron system is discussed as an illustration of the workability of the theory.

Currently there are several techniques available for calculating the ionisation potential (IP) and excitation energy (EE) of many electron systems which bypass separate calculations of the states of interest. Of these the more common are the propagator techniques [1], The Equation of Motion Method [2], and The Degenerate Many-Body Perturbation Theory [3]. Based on our recent non-perturbative cluster-expansion approaches [4, 5] for open-shell systems, we propose in this communication yet another method for calculating IP and EE of many-electron systems. The basic objective of this note is to explore the extent to which the non-perturbative formalism may be viewed as a direct method — paralleling the features of the methods mentioned above. The central idea is to employ a single cluster expansion operator e^T for correlating the states of interest required to calculate IP or EE. The energies of the various correlated states are then found to have a common part which drops out when difference in energies is taken [5]. We propose to choose the Hartree-Fock (HF) state for the ground state as the "vacuum" or "core". It then follows that the common energy part is just the exact ground state energy. We are thus led to expansion for IP or EE, in which the various quantities may be identified as correction to the corresponding quantities in the HF framework. An interesting feature of the method is that it includes in a natural way the effect of any class of important diagrams to all orders for which no well-defined algebraic series may be found [4]. This feature is not shared by the other methods mentioned [1, 2, 3].

We begin by choosing a "model space" spanned by a small number of determinantal states $\varphi_i(N)$ and $\varphi_i(N-1)$ which are needed to approximately describe the states of N and $N-1$ electron systems. The zeroth order description of the states of interest are given by

$$\psi_{\mathrm{K}}(N) = \sum_i c_{\mathrm{K}i}\, \varphi_i(N)\,, \tag{1a}$$

$$\psi_{\mathrm{K}'}(N-1) = \sum_i C_{\mathrm{K}'i}\, \varphi_i(N-1)\,, \tag{1b}$$

where we leave the coefficients unspecified for the present. A determinant obtained by replacing the spin-orbitals in φ_i's by excited orbitals will be said to belong to the "excited space". We are seeking an Ursell-type of cluster expansion operator e^T such that acting on the function of the type (1a) and (1b), it transforms each of them to the corresponding eigenfunction of H:

$$H\, e^T\, \psi_{\mathrm{K}}(N) = E_{\mathrm{K}}\, e^T\, \psi_{\mathrm{K}}(N)\,, \tag{2a}$$

$$H\, e^T\, \psi_{\mathrm{K}'}(N-1) = E_{\mathrm{K}'}\, e^T\, \psi_{\mathrm{K}'}(N-1)\,. \tag{2b}$$

We choose now the HF state as the "vacuum" $|0\rangle$ and the HF orbitals as the orbital set. The hole orbitals are designated as α, β, etc. and the particle orbitals as p, q etc. H can be represented as

$$H = E_{\mathrm{HF}} + \sum_A \varepsilon_A\, N[a_A{}^+ a_A] \qquad (3)$$
$$+ \frac{1}{2!^2} \sum_{\substack{A,B,\\C,D}} \langle AB|\,v\,|CD\rangle_a\, N[a_A{}^+ a_B{}^+ a_D\, a_C]$$

where N stands for normal ordering with respect to HF as the vacuum, and ε_A's are orbital energies for an orbital A. The capital Latin letters designate any orbital — hole or particle.

With the help of the Linked Cluster Theorem (LCT) for open-shells [4, 5], we may now define an effective operator $U \equiv U(T)$, such that

$$H\, e^T = e^T\, U\,. \qquad (4)$$

Equations (2) then yield:

$$U \sum_i C_{\mathrm{K}i}\, \varphi_i(N) = E_{\mathrm{K}} \sum_i C_{\mathrm{K}i}\, \varphi_i(N), \qquad (5\,\mathrm{a})$$

$$U \sum_i C_{\mathrm{K}'i}\, \varphi_i(N-1) = E_{\mathrm{K}'} \sum_i C_{\mathrm{K}'i}\, \varphi_i(N-1). \quad (5\,\mathrm{b})$$

Projecting Eqs. (5) on to the model-space functions, we have

$$\sum_i \langle \varphi_J(N)|\,U\,|\varphi_i(N)\rangle\, C_{\mathrm{K}i} = E_{\mathrm{K}}\, C_{\mathrm{K}J}\,, \qquad (6\,\mathrm{a})$$

$$\sum_i \langle \varphi_J(N-1)|\,U\,|\varphi_i(N-1)\rangle\, C_{\mathrm{K}'i} = E_{\mathrm{K}'}\, C_{\mathrm{K}'J}\,. \qquad (6\,\mathrm{b})$$

Equations (6) imply that the coefficients $C_{\mathrm{K}i}$ etc. are linearly independent, so that projecting (5) on to excited space, we have

$$\langle \varphi_l{}^*(N)|\,U\,|\varphi_i(N)\rangle = 0, \quad \text{for all } l \text{ and } i, \qquad (7\,\mathrm{a})$$

$$\langle \varphi_m{}^*(N-1)|\,U\,|\varphi_i(N-1)\rangle = 0, \quad \text{for all } m \text{ and } i. \qquad (7\,\mathrm{b})$$

Each set (7a) or (7b) form simultaneous coupled equations in the matrix-elements of T. For IP we employ (7a) with only one $\varphi_i(N)$ — the HF state, and (7b) for the $(N-1)$ electron determinants $\varphi_i(N-1)$. For EE, we employ (7a) only. $\varphi_i(N)$'s are the HF ground state and the singly excited determinants. Having found the matrix-elements of T, we employ them in (6a) or (6b), as the case may be, and get E_{K} or $E_{\mathrm{K}'}$.

So far we have made no special reference to IP or EE. In fact the detailed form of e^T will depend on whether we want IP or EE. For IP say, we choose the T-operator in such a manner that e^T can correlate both the N-electron ground state and the $(N-1)$-electron states. Taking the lowest ionic configuration as $a_\alpha|0\rangle$, for example, it suffices to include in T terms of the form

$$T = \sum_p T_p \qquad (8\,\mathrm{a})$$

with

$$T_p \sim \frac{1}{p!^2} \sum \langle p\,q \ldots|t_p|\gamma\,\delta \ldots\rangle_a \cdot N[a_p{}^+ a_q{}^+ \ldots a_\delta\, a_\gamma]$$
$$+ \frac{1}{p!^2} \sum \langle \alpha\, r \ldots|t_p|\gamma\,\delta \ldots\rangle_a \cdot N[a_\alpha{}^+ a_\gamma^+ \ldots a_\delta\, a_\gamma]$$
$$+ \frac{1}{p!^2} \sum \langle \alpha\, p \ldots|t_p|\alpha\,\gamma \ldots\rangle_a \cdot N[a_\alpha{}^+ a_p{}^+ \ldots a_\gamma\, a_\alpha]\,. \qquad (8\,\mathrm{b})$$

It is to be noted that, by virtue of the presence of an $a_\alpha{}^+$ in the third term this acts only on the one-hole state. The other two terms in operator however, act on both the N-electron and the one-hole states. The third term is needed to have two independent scattering amplitudes for the excitation $\gamma \ldots \to p \ldots$. A combination

$$\langle p \ldots|t_{p-1}|\gamma \ldots\rangle_a + \langle \alpha\, p \ldots|t_p|\alpha\,\gamma \ldots\rangle_a$$

would characterise this process for the one-hole state while $\langle p \ldots|t_{p-1}|\gamma \ldots\rangle$ only would be the analogous quantity for the HF state. A similar analysis applies to the case of EE. For greater details we refer to Ref. [5] and [6], where diagrammatic construction and handling of Eqs. (6) and (7) are discussed at length.

Now, for the calculation of the lowest IP, we have to evaluate $\langle 0|a_\alpha{}^+\, U\, a_\alpha|0\rangle$ and have to drop out the closed diagrams signifying the ground state energy. Similarly for the lowest EE, we have to diagonalise the matrix

$$\begin{bmatrix} \langle \varphi_1|\,U\,|\varphi_1\rangle & \langle \varphi_1|\,U\,|\varphi_2\rangle \\ \langle \varphi_2|\,U\,|\varphi_1\rangle & \langle \varphi_2|\,U\,|\varphi_2\rangle \end{bmatrix},$$

and omit the closed-diagrams once again. As for EE, with model space functions φ_1 and φ_2 chosen as components comprising spin-eigen-functions for the excited states, the coefficients are determined by symmetry, we have

$$E_{\mathrm{s,t}} = \langle \varphi_1|\,U\,|\varphi_1\rangle \pm \langle \varphi_1|\,U\,|\varphi_2\rangle \qquad (9)$$

where the $+$ (-1) sign refers to the singlet (triplet) EE.

We have tested the applicability of the theory by calculating the lowest IP and EE of trans-butadiene molecule in the PPP model. We have kept in U only those terms which are at most linear in T and we keep operators with $p \geqq 2$ for the first and second type of terms in (8b) and $p \geqq 3$ for the third type. The results are collected in Table 1, where we have shown the full CI results as well for assessing the performance. The agreement is very good.

The related aspects of the core-valence separation and relation with perturbative open-shell theories and propagator methods is being published elsewhere [6].

Table 1. The π-π^* singlet and triplet EE and the lowest IP of trans-butadiene in eV.

Quantity	Present results	Full CI results
IP	11.678	11.683
Singlet EE	6.534	6.548
Triplet EE	3.744	3.685

[1] See, e.g. J. Linderberg and Y. Öhrn, Propagators in Quantum Chemistry, Academic Press, New York 1973.
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