

# A Evaluation of Excitation Energies of Doublet Radicals from One-Particle Green's Functions

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一粒子グリーン関数から二重項ラジカルの  
励起エネルギーを評価する一方法

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原子や分子の励起エネルギーは、一般には、二粒子グリーン関数に関係した量と考えられているが、話を二重項ラジカルに限れば、レーマン展開における発散点の性質を利用することにより、一粒子グリーン関数から励起エネルギーを評価することが、可能である。その一方法が、述べられ、試験的計算および若干のリマークが、付け加えられる。

## INTRODUCTION

For the system of electrons in the fixed nuclear framework we may put the Hamiltonian as

$$H = \sum_{pq\sigma} h_{pq} a_{p\sigma}^\dagger a_{q\sigma} + \frac{1}{2} \sum_{pqrs} v_{qs}^{pr} a_{p\sigma}^\dagger a_{r\tau}^\dagger a_{s\tau} a_{q\sigma}, \quad (1)$$

where  $a_{p\sigma}^\dagger$  and  $a_{p\sigma}$  are, respectively, the creation and annihilation operators for the one-electron quantum state  $p\sigma$ ,  $\sigma$  standing for the spin. By going to a relevant basis, for example the Hartree-Fock(HF) one, (1) is rewritten as the sum of the unperturbed Hamiltonian

$$H_0 = \sum_{j\sigma} \epsilon_j b_{j\sigma}^\dagger b_{j\sigma}$$

and the perturbation

$$H' = \frac{1}{2} \sum_{\substack{jklm \\ \sigma\tau}} V_{km}^{jl} b_{j\sigma}^\dagger b_{l\tau}^\dagger b_{m\tau} b_{k\sigma} - \sum_{jk\sigma} X_{jk} b_{j\sigma}^\dagger b_{k\sigma}.$$

Then, it is almost exclusively useful to define the one-particle Green's function in the frequency-dependent matrix form as

$$\mathbf{G}(\epsilon) = \{G_{jk}(\epsilon)\} \quad (2)$$

with

$$G_{jk}(\epsilon) = (-i) \int e^{i\epsilon(t-t')} d(t-t') \langle No | T b_{j\sigma} [t] b_{k\sigma}^\dagger [t'] | No \rangle, \quad (3)$$

where  $T$  is Wick's time-ordering operator,  $|No\rangle$  stands for the  $N$ -electron ground state of  $H$ , and

$$\begin{cases} b_{j\sigma} [t] = e^{iHt} b_{j\sigma} e^{-iHt} \\ b_{k\sigma}^\dagger [t'] = e^{iHt'} b_{k\sigma}^\dagger e^{-iHt'} \end{cases}.$$

Denoting the  $N$ -electron  $n$ -th eigenstate of  $H$  and its eigenvalue by  $|Nn\rangle$  and  $E_n^N$ , respectively, and expanding (3) as

$$G_{jk}(\epsilon) = \sum_n \left\{ \frac{\langle No | b_{j\sigma} | N+1n \rangle \langle N+1n | b_{k\sigma}^\dagger | No \rangle}{\epsilon - (E_n^{N+1} - E_o^N) + i\Delta} + \frac{\langle No | b_{k\sigma}^\dagger | N-1n \rangle \langle N-1n | b_{j\sigma} | No \rangle}{\epsilon + (E_n^{N-1} - E_o^N) - i\Delta} \right\},$$

we see that  $\mathbf{G}(\epsilon)$  is divergent at the following frequencies<sup>1)</sup>;

$$\epsilon^-(n) = E_n^{N+1} - E_o^N - i\Delta \quad (4)$$

and

$$\epsilon^+(n) = E_o^N - E_n^{N-1} + i\Delta \quad (5)$$

with a positive infinitesimal  $\Delta$ . On the other hand,  $\mathbf{G}(\epsilon)$  is ready to be expressed in terms of the unperturbed one-particle Green's function,  $\mathbf{G}^0(\epsilon)$ , and the proper self-energy part,  $\mathbf{S}(\epsilon)$ , as

$$\mathbf{G}(\epsilon) = \{\mathbf{G}^0(\epsilon)^{-1} - \mathbf{S}(\epsilon)\}^{-1},$$

so that we can obtain the poles of  $\mathbf{G}(\epsilon)$  directly from

$$|\mathbf{G}^0(\epsilon)^{-1} - \mathbf{S}(\epsilon)| = 0. \quad (6)$$

The concrete definitions of  $\mathbf{G}^0(\epsilon)$  and  $\mathbf{S}(\epsilon)$  are obvious from that of  $\mathbf{G}(\epsilon)$ , (2) with (3), and omitted for brevity. The most orthodox utilization of (4), (5), and (6) in the field of molecular quantum mechanics is found in the evaluations of vertical ionization potentials and electron affinities.<sup>2)</sup>

What one calls excitation energies of atoms and molecules are, in general, thought to be the quantities concerning two-particle Green's functions, and there exist already several remarkable studies along the line.<sup>3)</sup> However, unfortunately it seems very difficult to go beyond the random phase approximation (RPA)<sup>4)</sup> or 'modified' RPA methods<sup>3)</sup> by means of two-particle Green's functions.

Confining ourselves to doublet radicals, we become aware of a method of evaluation of the excitation energies from one-particle Green's functions. Of course, we never intend to assert that the method can go to or beyond RPA with ease, but only hope that those groupings in the perturbation series of one-particle Green's functions may be devised which give physically interesting results. Although the analysis is not completed, we think the method is worth communicating.

## METHOD AND TENTATIVE CALCULATION

Returning to (4) and focussing our attention upon the two pole frequencies,

$$\epsilon^-(n) = E_n^{N+1} - E_v^N - i\Delta$$

and

$$\epsilon^-(o) = E_o^{N+1} - E_o^N - i\Delta,$$

we see that the difference between them results in the excitation energy of the  $N+1$ -electron system,  $\omega_n$ ;

$$\omega_n = E_n^{N+1} - E_o^{N+1} = \epsilon^-(n) - \epsilon^-(o). \quad (7)$$

This relation is the keystone of the whole story.

Now let us take a doublet radical of  $N+1$  electrons,  $N$  being an even number. The excitation energies of the radical can be obtained through (7) from the knowledge of the pole frequencies of  $\mathbf{G}(\epsilon)$ , the one-particle Green's function for the  $N$ -electron system. Since  $N$  is even, we can make the ground state of  $H_o$  be the Fermi sea in which each orbital below the Fermi level is doubly-occupied by the two electrons in the different spin states. The procedures are summarized as follows.

- i) Define  $\mathbf{G}^o(\epsilon)$  for the closed system of  $N$  electrons in the nuclear framework of the  $N+1$ -electron radical in question.
- ii) Calculate  $\mathbf{S}(\epsilon)$  under the relevant approximation.
- iii) Solve (6), obtaining the roots in the lower-half plane.
- iv) Take appropriate differences between the roots obtained in iii).

Note that  $\{h_{pq}\}$  in (1) should be the matrix elements having the values in the radical nuclear framework. How to select a set of the one-electron quantum states  $\{p\sigma\}$  is very important, but another problem.

Only to see how our method works tentative calculation was carried out on the allyl radical in the Pariser-Parr-Pople (PPP) model. Putting

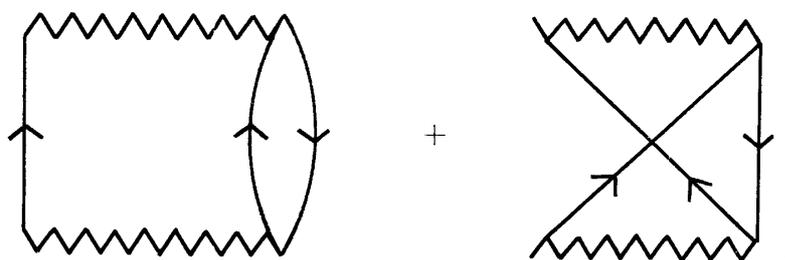
$$v_{qs}^{pr} = \delta_{pq} \delta_{rs} \gamma_{pr} \quad \{p\} = \{1, 2, 3\}$$

in (1) and using the parameter values adopted by Longuet-Higgins and Pople in their PPP calculation of the allyl radical and cation,<sup>5)</sup>  $\gamma_{11} = \gamma_{22} = \gamma_{33} = 10.53eV$ ,  $\gamma_{12} = \gamma_{23}$

$= 7.30eV$ ,  $\gamma_{13} = 5.46eV$ ,  $h_{12} = h_{23} = -2.39eV$ ,  $h_{13} = 0$ , and  $h_{11} = h_{22} = h_{33} = W$ , we had the HF orbitals of energies  $\epsilon_1 = -0.50eV + W$ ,  $\epsilon_2 = 8.68eV + W$ , and  $\epsilon_3 = 13.64eV + W$ ,  $\mathbf{G}^0(\epsilon)^{-1}$  being given by

$$\mathbf{G}^0(\epsilon)^{-1} = \begin{pmatrix} \epsilon - \epsilon_1 - i\Delta & 0 & 0 \\ 0 & \epsilon - \epsilon_2 + i\Delta & 0 \\ 0 & 0 & \epsilon - \epsilon_3 + i\Delta \end{pmatrix}.$$

Hence, the excitation energy  $\omega = 4.96eV$  was obtained as the  $\mathbf{S}(\epsilon) = 0$  result. The first non-vanishing contribution to  $\mathbf{S}(\epsilon)$  in the HF basis appears in the second order;



which is translated in the present case by virtue of the symmetry into

$$\mathbf{S}(\epsilon) = \begin{pmatrix} S_{11}(\epsilon) & 0 & S_{13}(\epsilon) \\ 0 & S_{22}(\epsilon) & 0 \\ S_{31}(\epsilon) & 0 & S_{33}(\epsilon) \end{pmatrix},$$

with

$$S_{11}(\epsilon) = \frac{V_{22}^{21^2}}{\epsilon - (2\epsilon_2 - \epsilon_1) + i\Delta} + \frac{V_{33}^{11^2}}{\epsilon - (2\epsilon_3 - \epsilon_1) + i\Delta} + \frac{V_{13}^{11^2}}{\epsilon - (2\epsilon_1 - \epsilon_3) - i\Delta},$$

$$S_{22}(\epsilon) = \frac{2(V_{23}^{21^2} + V_{32}^{21^2} - V_{23}^{21} V_{32}^{21})}{\epsilon - (\epsilon_2 + \epsilon_3 - \epsilon_1) + i\Delta} + \frac{V_{22}^{11^2}}{\epsilon - (2\epsilon_1 - \epsilon_2) - i\Delta},$$

$$S_{33}(\epsilon) = \frac{V_{32}^{21^2}}{\epsilon - (2\epsilon_2 - \epsilon_1) + i\Delta} + \frac{V_{31}^{33^2}}{\epsilon - (2\epsilon_3 - \epsilon_1) + i\Delta} + \frac{V_{33}^{11^2}}{\epsilon - (2\epsilon_1 - \epsilon_3) - i\Delta},$$

and

$$S_{13}(\epsilon) = S_{31}(\epsilon) = \frac{V_{22}^{11} V_{32}^{21}}{\epsilon - (2\epsilon_2 - \epsilon_1) + i\Delta} + \frac{V_{33}^{11} V_{31}^{33}}{\epsilon - (2\epsilon_3 - \epsilon_1) + i\Delta} + \frac{V_{33}^{11} V_{13}^{11}}{\epsilon - (2\epsilon_1 - \epsilon_3) - i\Delta}.$$

Taking account of this frequency-dependent contribution, we saw the several excitation energies arise;  $\omega/eV = 4.68, 4.85, 5.01$ , and so on. Although no energy-level scheme rivalling to that obtained by the configuration interaction method<sup>5)</sup> or the atoms-in-molecule method,<sup>6)</sup> it is not very discouraging considering the stage of approximation. By the way, another parameter choice that  $\gamma_{11} = \gamma_{22} = \gamma_{33} = 10.84eV$ ,  $\gamma_{12} = \gamma_{23} = 5.44eV$ ,  $\gamma_{13} = 3.98eV$ ,  $h_{12} = h_{23} = -2.60eV$ ,  $h_{13} = -0.41eV$ ,  $h_{11} = h_{33} = W$ , and  $h_{22} = W - 1.89eV$  led us to  $\omega/eV = 3.37, 3.44, 6.50$ , and so on. We have no interest in the parameter manipulation here.

## SUPPLEMENTARY REMARKS

It may favor our understanding of the method to add some supplementary remarks in the rest.

### A) Hole Potential

Taking the HF basis with the vanishing self-energy part, we immediately obtain  $\{|\epsilon_j - \epsilon_k|\}$  as the excitation energies of the  $N+1$ -electron radical,  $j$  and  $k$  being vacant in  $|NF\rangle$ , the  $N$ -electron ground state of  $H_0$ . Thus it is suggested that our method is closely related to the hole potential method<sup>7)</sup>; an electron in  $j$  or  $k$  feels the average field due to  $N$  electrons in the orbitals occupied in  $|NF\rangle$ .

## B) Hydrogen Atom

It is rather trivial but instructive to apply the method to the simplest system, the hydrogen atom. This is the  $N=0$  case and we have merely a bare proton in the electron vacuum  $|0F\rangle$ . Because no self-energy part exists, (6) together with (4) and (7) gives the excitation energies of the 1-electron system as  $\{|\epsilon_j - \epsilon_k|\}$ ,  $\{\epsilon_j\}$  being a set of the orbital energies of the hydrogen atom. The correct result is obtained.

## C) Technical Merits

The technical merits of our method include the ones in common with any Green's function approach using the Feynman-Dyson perturbation theory; use of the Dyson type equation, control of approximation through the proper self-energy part, availability of the diagrammatic language, and so on. However, it is the most remarkable that we may work on the 'closed' and 'one-less-particle' system.

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