

A Handy Evaluation of Excitation Energies of Molecules with Electron-Pair Propagators (Preliminary Note)

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電子対伝播関数による分子の励起エネルギーの
簡便評価法 (予報)

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Singlet and triplet excitation energies from a closed-shell ground state of a system of N electrons are shown to be obtainable as distances between poles of electron-pair propagators defined with an $N-2$ -electron state. A determinantal equation giving the poles is derived to the approximation taking the first order scattering kernel into account in a Dyson type equation for the electron-pair propagators. The advantage of the method is clarity of the spin treatment and sound nature of the orbitals used there.

Many of Molecules have electronic level structures consisting of a closed-shell ground and low-lying singlet and triplet excited states. Confining ourselves to such systems, we propose a handy method to evaluate the excitation energies.

Consider a system of N (an even number) electrons in a fixed nuclear framework, whose Hamiltonian is assumed to be

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

where $a_{p\sigma}^+$ and $a_{p\sigma}$ are, respectively, the creation and annihilation operators for the one-electron quantum state $p\sigma$, the second suffix σ referring to the spin. Taking a relevant hermitian one-electron operator

$$X = \sum_{pq\sigma} x_{pq} a_{p\sigma}^+ a_{q\sigma},$$

going through an eigenvalue problem

$$\sum_q (h_{pq} + x_{pq}) u_{qj} = u_{pj} \epsilon_j,$$

we rewrite the Hamiltonian in the molecular orbital representation as a sum of the unperturbed Hamiltonian

$$H^0 = \sum_{j\sigma} \epsilon_j a_{j\sigma}^+ a_{j\sigma}$$

and the perturbation

$$H' = \frac{1}{2} \sum_{jklm\sigma\tau} v_{km}^{jl} a_{j\sigma}^{\dagger} a_{l\tau}^{\dagger} a_{m\tau} a_{k\sigma} - \sum_{jk\sigma} x_{jk} a_{j\sigma}^{\dagger} a_{k\sigma}.$$

Selection of X is postulated to be restricted so as to give clear correspondence between the resultant molecular orbitals and the Hückel or Hartree-Fock orbitals; this allows us to use an identical set of the molecular orbital indices. We denote a set of the $N/2$ occupied orbital indices by F and that of the unoccupied by \bar{F} .

Now suppose that an excitation in question can be specified by a combination of $f \in F$, $g \in \bar{F}$, and the multiplicity (singlet or triplet). Let C be a set of the $(N-2)/2$ occupied orbitals except f and take the normalized $N-2$ -electron eigenstate of H^o of a doubly occupied configuration

$$|C\rangle = \prod_{j \in C} a_{j\uparrow}^{\dagger} a_{j\downarrow}^{\dagger} |\text{vacuum}\rangle,$$

where \uparrow and \downarrow stand for the up- and down-spin states respectively. Denoting the corresponding $N-2$ -electron eigenstate of H by $|\tilde{C}\rangle$ and introducing the singlet and triplet electron-pair operators

$${}^1b_{jk}^{\dagger} = (a_{j\uparrow}^{\dagger} a_{k\downarrow}^{\dagger} + a_{k\uparrow}^{\dagger} a_{j\downarrow}^{\dagger}) / \sqrt{2} \quad (j < k),$$

$${}^1b_{jj}^{\dagger} = a_{j\uparrow}^{\dagger} a_{j\downarrow}^{\dagger},$$

and

$${}^3b_{jk}^{\dagger} = (a_{j\uparrow}^{\dagger} a_{k\downarrow}^{\dagger} - a_{k\uparrow}^{\dagger} a_{j\downarrow}^{\dagger}) / \sqrt{2} \quad (j \leq k)$$

together with

$${}^M b_{jk} = ({}^M b_{jk}^{\dagger})^{\dagger},$$

we define electron-pair propagators as

$$i{}^M P_{j\downarrow k m}(t-t') = \langle \tilde{C} | T^M b_{j\downarrow} [t] {}^M b_{k m}^{\dagger} [t'] | \tilde{C} \rangle / \langle \tilde{C} | \tilde{C} \rangle,$$

where operators having the time argument in the square bracket are in the Heisenberg picture, T being Wick's chronological operator. The Lehmann expansion⁽¹⁾ shows that the Fourier transform

$${}^M P_{j\downarrow k m}(E) = \int {}^M P_{j\downarrow k m}(t-t') \exp(iE(t-t')/\hbar) d(t-t')/\hbar$$

has poles in the lower-half plane at

$$E = {}^M E_N^{\mu} - E_{N-2} - i\eta,$$

where ${}^M E_N^{\mu}$ is the energy of the N -electron μ th eigenstate of the multiplicity M and E_{N-2} is that of $|\tilde{C}\rangle$, η standing for a positive infinitesimal number. Thus we can evaluate the excitation energies in the N -electron system as distances between these poles without regard to the detailed knowledge of the states concerned. The poles in the upper-half plane are related with $N-4$ -electron states and have nothing to do with the present purpose.

The definition of the unperturbed electron-pair propagators is obvious from that of the

perturbed ; the Fourier transforms are given by

$${}^M P_{j:l;km}^o(E) = \delta_{jk} \delta_{lm} (1 - \delta_{M3} \delta_{jl}) \left(\frac{\bar{\gamma}(j) \bar{\gamma}(l)}{E - (\epsilon_j + \epsilon_l) + i\eta} - \frac{\gamma(j) \gamma(l)}{E - (\epsilon_j + \epsilon_l) - i\eta} \right)$$

with

$$\gamma(j) = \begin{cases} 1 & (j \in C) \\ 0 & (j \notin C) \end{cases}$$

and

$$\bar{\gamma}(j) = 1 - \gamma(j).$$

Note that the unperturbed electron-pair propagators are not only diagonal with respect to the pair indices but also vanishing for such pairs as $j \in C$ and $l \notin C$.

It is presumably most reasonable in many cases to determine the molecular orbitals self-consistently by setting

$$x_{pq} = \sum_{j \in C} (2v_{qj}^{pj} - v_{jq}^{pj}).$$

Then, neither the tadpole diagram nor the open oyster one appears in the Feynman expansion of the electron-pair propagators.⁽²⁾ Using the first order proper scattering kernel of the matrix elements

$${}^1 K_{j:l;km} = \begin{cases} v_{km}^{jl} + v_{mk}^{jl} & (j < l, k < m) \\ \sqrt{2} v_{km}^{jj} & (j = l, k < m) \\ \sqrt{2} v_{kk}^{jl} & (j < l, k = m) \\ v_{kk}^{jj} & (j = l, k = m) \end{cases}$$

and

$${}^3 K_{j:l;km} = \begin{cases} v_{km}^{jl} - v_{mk}^{jl} & (j < l, k < m) \\ 0 & (j = l \text{ and/or } k = m), \end{cases}$$

we can write a Dyson type equation in the matrix form as

$${}^M \mathbf{P}(E) = {}^M \mathbf{P}^o(E) + {}^M \mathbf{P}^o(E) {}^M \mathbf{K} {}^M \mathbf{P}(E)$$

with

$${}^M \mathbf{P}(E) = ({}^M P_{j:l;km}(E))$$

and so on, where the component indices run over $j \leq l, k \leq m$ for $M = 1$ and $j < l, k < m$ for $M = 3$.

The poles are hence obtained from a simple determinantal equation :

$$\text{Det} | {}^M \mathbf{P}^o(E)^{-1} - {}^M \mathbf{K} | = 0.$$

If we neglect all the off-diagonal elements of ${}^M \mathbf{K}$, the poles of interest in the lower-half plane are immediately seen to stay at

$$E = 2\epsilon_f + v_{ff}^{ff} - i\eta$$

and

$$E = \epsilon_f + \epsilon_g + v_{fg}^{fg} \pm v_{gf}^{fg} - i\eta \quad (g \in \bar{F}).$$

The resultant expression of the excitation energy ΔE from the N -electron closed-shell ground state to the singlet or triplet excited state has the same form as obtained in a primitive orbital picture :

$$\Delta E = \varepsilon_g - \varepsilon_f + v_{fg}^{fg} - v_{ff}^{ff} \pm v_{gf}^{fg}.$$

Result of tentative calculation is shown in Table I for the pi-electron system of *cis*-butadiene. The LCAO MO's are named 1, 2, 3, and 4 in energy-increasing order. Taking the $N-2$ -electron state

$$|C\rangle = a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger | \text{vacuum} \rangle ,$$

we can obtain the singlet and triplet excitation energies specified by an occupied orbital 2 and an unoccupied orbital 3 or 4, which are denoted by ${}^1(2 \rightarrow 3)$, ${}^3(2 \rightarrow 4)$, and so on. The basis is four $2p\pi$ Slater type orbitals with an identical exponent ξ , the approximate atomic integrals given by Parr and Mulliken⁽³⁾ being adopted for the sake of comparison. The calculated excitation energy ${}^1(2 \rightarrow 3)$ varies slowly as ξ does, and is about 2eV smaller than that of Parr and Mulliken's SCF result,⁽³⁾ nearing the experimental value, a little smaller than 6eV. We have the lowering also for ${}^1(2 \rightarrow 4)$ about 3eV, which seems to be good inclination.

Although the above mentioned method allows us to evaluate only excitation energies of a restricted class under certain specific choice of $|C\rangle$ (*i. e.* C) and gives no knowledge of transition intensities, it has advantage that the orbitals used have physically sound nature⁽⁴⁾ and that the treatment of the spin state is simple and clear⁽⁵⁾.

Table I. Excitation energies of *cis*-butadiene ($\Delta E/\text{eV}$)

methods		${}^1(2 \rightarrow 3)$	${}^1(2 \rightarrow 4)$	${}^3(2 \rightarrow 3)$	${}^3(2 \rightarrow 4)$
proposed	$\xi = 1.59$	5.69	7.95	2.76	7.08
	1.6	5.70	7.96	2.77	7.06
	1.7	5.75	7.96	2.78	6.85
	1.8	5.76	7.85	2.70	6.55
	1.9	5.73	7.68	2.57	6.24
diagonal approximation	$\xi = 1.59$	8.12	10.94	2.48	6.66
	1.6	8.14	10.91	2.48	6.64
	1.7	8.32	10.60	2.45	6.39
	1.8	8.45	10.24	2.33	6.06
	1.9	8.52	9.87	2.15	5.68
Parr-Mulliken	$\xi = 1.59$	7.80	11.13	3.01	6.54
experimental		6.0			

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