Excitation and Wave Function of a Molecular System in RPA

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The random phase approximation (RPA) is very successful in describing the behaviour of nuclei (for references see1). The RPA has been applied to a molecular system very recently2. The aim of our work is to describe a different way of obtaining the set of equations describing the excitation in a molecular system. The discussion of the wave function is also included.

The idea is to find the RPA Hamiltonian and to obtain from it all valuable informations. The exact Hamiltonian written in second quantization is:

$$H = \sum_{s} e_{s} a_{s}^{\dagger} a_{s} + \frac{1}{2} \sum_{s t s' t'} \tilde{V}_{s t s' t'} a_{t}^{\dagger} a_{s}^{\dagger} a_{s} a_{t} - \sum_{s t} U_{s t} a_{s}^{\dagger} a_{t}$$

(1)

where the Hartree-Fock Hamiltonian is explicitly introduced:

$$\sum_{s t} (T_{s t} + U_{s t}) a_{s}^{\dagger} a_{t} = \sum_{s} e_{s} a_{s}^{\dagger} a_{s}$$

(2)

with

$$U_{s t} = \sum_{s' ss' ts'} V_{s s' ts'}$$

$$V_{s s' ts'} = \tilde{V}_{s s' ts'} - \tilde{V}_{ss' ts'}$$

and

$$\tilde{V}_{ijkl} = \int q_{i}^{*} (1) q_{j}^{*} (2) \frac{1}{r_{12}} q_{k} (1) q_{l} (2) dv_{1} dv_{2}$$

By introducing the particle — hole scheme3 (the particles are denoted i, j, k... and the holes m, n...) and the following particle — hole creation and annihilation operators

$$B^{+} (im) = a_{i}^{\dagger} a_{m}, \quad B (im) = a_{m}^{\dagger} a_{i}$$

(4)

which are treated as ideal boson operators and thus satisfy strictly

$$[B (im), B^{+} (jn)] = \delta_{ij} \delta_{mn}$$

$$[B (im), B (jn)] = [B^{+} (im), B^{+} (jn)] = 0$$

(5)
the Hamiltonian eq. (1) can be written in terms of $B^+ (im) B (jn)$. The RPA Hamiltonian results from this expression if only terms linear in boson operators are retained:

$$H_{\text{RPA}} = E_{\text{HF}} + \sum_{im} (e_i - e_m) B^+ (im) B (im) + \sum_{im, ij} (V_{jm, ui} \cdot)$$

\[
\cdot B^+ (jn) B (im) + \frac{1}{2} V_{im, ij} B (jn) B (im) + \frac{1}{2} V_{ij, mn} \cdot B^+ (mi) B^+ (nj) \] (6)

where $E_{\text{HF}}$ is the Hartree-Fock ground state energy. We note an interesting property of $H_{\text{RPA}}$: the quasi-particles (the diagonal part of $H_{\text{RPA}}$) are single excitations with the same energy as obtained by Roothaan$^4$ with the SCF theory. The non-diagonal part of $H_{\text{RPA}}$ describes the interaction between quasi-particles and with its diagonalization the so-called collective vibrations are obtained.

The diagonalization of $H_{\text{RPA}}$ is made with the operator $Q^+_p$ which satisfies$^5$:

$$[H_{\text{RPA}}, Q_p^-] = \omega_p Q^+_p$$ (7)

and commutator relations

$$[Q_p, Q^+_p] = \delta_{pq} \quad [Q_p, Q^-_q] = [Q^+_p, Q_q^-] = 0$$

The following ansatz for $Q^+_p$ is made$^6$

$$Q^+_p = \sum_{im} (X^p (im) B^+ (im) + Y^p (im) B (im))$$ (8)

From eq. (7) and (8) the set of equation results:

$$(e_i - e_m) X^p (im) + \sum_{jn} (V_{in, mj} X^p (jn) - V_{ji, nm} Y^p (jn)) = \omega_p X^p (im)$$

$$(e_i - e_m) Y^p (im) + \sum_{jn} (V_{in, mj} Y^p (jn) - V_{ji, nm} X^p (jn)) = -\omega_p Y^p (im)$$ (9)

The eqs. (9) determine excitation energy $\omega_p$ and the coefficients $X$ and $Y$. The set of eqs. (9) is the same as can be found in literature$^2,7,8$. Once the operator $Q_p$ is known, the ground state wave function $|0> = v_0$ is evaluated from$^5$:

$$Q_p |0> = 0$$ (10)

The wave function $|O> = v_0 |HF> + \sum_{im} b_i (im) B^+ (im) |HF> + \sum_{im, jm} b_{ij} (im, jm) B^+ (im) B^+ (jm) |HF> + \ldots$$ (11)

We use the fact that the vacuum state for the operators $B (i, m)$ is just the Hartree-Fock ground state. The coefficients $b_i$ can be evaluated from eq. (10). From this it follows that only the terms with 0, 2, 4 ... quasi-particles occur and the recurrence relations between $b_i$ and $b_{i+2}$ exist. In the lowest order the wave function is given by:

$$|O> = b_0 |HF> + \sum_{im, jm} b_{2} (im, jm) B^+ (im) B^+ (jm) |HF> + \ldots$$ (12)
which is the same as obtained from the configuration interaction treatment. A very good approximation for $b_2$ is:

$$b_2 (im, jn) = \frac{b_0}{2} \sum_p Y^p (jn) X^p (im)$$

The operators $B(i,m)$ were treated as ideal boson operators and the Fermi principle was not taken into account. This can be treated in a way which seems to be very complicated\textsuperscript{9,10} but the method described recently by Wallace\textsuperscript{11} is much more appropriate.

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REFERENCES


IZVLEČEK

Valovna funkcija in eksitacija molekulskega sistema s RPA metodo

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Pokazana je uporaba RPA (random phase approximation) metode na molekulsko sisteme. Upeljan je Hamiltonian, ki vsebuje samo linearno kvazidelčne operatorje in je enak RPA Hamiltonianu. Pokazana je enakost diagonalnega dela Hamiltoniana s enodelčnimi eksitacijami in zveza med osnovnim stanjem RPA Hamiltoniana in metodo konfiguracije interakcij.

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