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Note

Excitation and Wave Function of a Molecular System in RPA*A. Ocvirk and A. Ažman**Department of Chemistry, University of Ljubljana, and Chemical Institute
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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:

$$H = \sum_s e_s a_s^+ a_s + 1/2 \sum_{sts't'} \tilde{V}_{sts't'} a_t^+ a_s^+ a_{s'} a_{t'} - \sum_{st} U_{st} a_s^+ a_t \quad (1)$$

where the Hartree-Fock Hamiltonian is explicitly introduced:

$$\sum_{st} (T_{st} + U_{st}) a_s^+ a_t = \sum_s e_s a_s^+ a_s \quad (2)$$

with

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

and

$$\tilde{V}_{ijkl} = \int \varphi_i^*(1) \varphi_j^*(2) \frac{1}{r_{12}} \varphi_k(1) \varphi_l(2) dv_1 dv_2$$

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

$$B^+(im) = a_i^+ a_m, \quad B(im) = a_m^+ a_i \quad (4)$$

which are treated as ideal boson operators and thus satisfy strictly

$$\begin{aligned} [B(im), B^+(jn)] &= \delta_{ij} \delta_{mn} \\ [B(im), B(jn)] &= [B^+(im), B^+(jn)] = 0 \end{aligned} \quad (5)$$

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

$$H_{RPA} = E_{HF} + \sum_{im} (e_i - e_m) B^+(im) B(im) + \sum_{ijmn} (V_{jm, ni} \cdot B^+(jn) B(im) + 1/2 V_{mn, ij} B(jn) B(im) + 1/2 V_{ij, mn} \cdot B^+(mi) B^+(nj)) \quad (6)$$

where $E_{H.F.}$ is the Hartree-Fock ground state energy. We note an interesting property of H_{RPA} : the quasi-particles (the diagonal part of H_{RPA}) are single excitations with the same energy as obtained by Roothaan⁴ with the SCF theory. The non-diagonal part of H_{RPA} describes the interaction between quasi-particles and with its diagonalization the so-called collective vibrations are obtained.

The diagonalization of H_{RPA} is made with the operator Q_p^+ which satisfies⁵:

$$[H_{RPA}, Q_p^+] = \omega_p Q_p^+ \quad (7)$$

$$[H_{RPA}, Q_p] = -\omega_p Q_p$$

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 made⁶

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

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

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

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

The eqs. (9) determine excitation energy ω_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 $|0\rangle$ is evaluated from⁵:

$$Q_p |0\rangle = 0 \quad (10)$$

The wave function $|O\rangle$ can be approximated with some known wave function and the following expansion is made:

$$|O\rangle = b_0 |HF\rangle + \sum_{im} b_1(im) B^+(im) |HF\rangle + \sum_{im, jn} b_2(im, jn) B^+(im) B^+(jn) |HF\rangle + \dots \quad (11)$$

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:

$$|O\rangle = b_0 |HF\rangle + \sum_{im, jn} b_2(im, jn) B^+(im) B^+(jn) |HF\rangle + \dots \quad (12)$$

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^{9,10} but the method described recently by Wallace¹¹ is much more appropriate.

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REFERENCES

1. Da Providencia, *Nuclear Physics A* **108** (1968) 589.
2. T. H. Dunning and V. McKoy, *J. Chem. Phys.* **47** (1967) 1735.
3. D. J. Thouless, *The Quantum Mechanics of Many-Body Systems*, Academic Press, New York 1961.
4. C. C. J. Roothaan, *Rev. Mod. Phys.* **23** (1951) 69.
5. D. Pines, *The Many-Body Problem*, W. A. Benjamin 1962.
6. M. Baranger, *Phys. Rev.* **120** (1960) 957.
7. D. J. Thouless, *Nuclear Physics* **22** (1961) 78.
8. P. L. Altick and A. E. Glassgold, *Phys. Rev.* **133** (1964) 632.
9. K. Hara, *Progress of Theoretical Physics* **32** (1964) 88.
10. K. Ikeda, T. Udagawa and H. Yamaura, *Progress of Theoretical Physics* **33** (1965) 22.
11. D. C. Wallace, *Phys. Rev.* **152** (1966) 247.

IZVLEČEK

Valovna funkcija in eksitacija molekulskega sistema s RPA metodo

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Pokazana je uporaba RPA (random phase approximation) metode na molekulske 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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