

CCA-572

539.19

Note

HFB-SCF-RPA Treatment of Molecular Excitations

B. Lukman and A. Ažman

*Department of Chemistry, University of Ljubljana and Chemical Institute
Boris Kidrič, Ljubljana, Slovenia, Yugoslavia*

Received July 21, 1969

Very recently the Hartree-Fock-Bogoliubov self-consistent-field (HFB-SCF) method was applied to molecular systems¹. It was shown that the energy is not an appropriate quantity to show to which extent the pairing interaction is involved and the suggestion was given that perhaps other quantities are more sensitive. In recent time the RPA² with the Hartree-Fock ground state wave function as the zero order wave function has proved to be very successful in calculating the excitation energies of molecules. We expect even better results with RPA using the HFB ground state wave function as zero order wave function. In this paper we would like to write down explicitly the expression necessary to calculate transition energies. As far as we know such an evaluation has not been done before though the general prescription is well known. The procedure we used is due to Baranger³.

The form of the Hamiltonian after Bogoliubov's transformation is (1):

$$H' = H_1 + H_2 + H_3 + H_4 \quad (1)$$

With

H_1 = energy of the ground state (pure number)

$$H_2 = \sum_a E_a a_a^+ a_a$$

$$H_3 = 0$$

$$H_4 = 1/4 \sum_{klmn} V_{klmn} N_a (c_k^+ c_l^+ c_n c_m)$$

E_a and coefficients A and B are determined in self-consistent manner¹.

Independent excitations of the system are described by the operators:

$$A^+(ij) = a_i^+ a_j^+$$

$$A(ij) = a_j a_i \quad (2)$$

Only pairs of the quasi-particles operators have to be used because the condition of the fixed number of quasi-particles has to be satisfied.

The operators that describe collective excitation are combinations of A^+ , and A . They satisfy the Heisenberg equation:

$$\begin{aligned} [Q_B, H'] &= \omega_B Q_B \\ [Q_B^+, H'] &= -\omega_B Q_B^+ \end{aligned} \quad (3)$$

where ω is the excitation energy. Q and Q^+ are supposed to be of the form:

$$\begin{aligned} Q_B &= \sum_{ij} X_{ijB} A(ij) - \sum_{ij} Y_{ijB} A^+(ij) \\ Q_B^+ &= \sum_{ij} X_{ijB} A^+(ij) - \sum_{ij} Y_{ijB} A(ij) \end{aligned} \quad (4)$$

In this case equation (3) gives in RPA approximation the coupled equations for the coefficients X and Y :

$$\begin{aligned} \omega_B X_{ijB} &= \sum_{kl} P(ij, kl) X_{klB} + \sum_{kl} R(ij, kl) Y_{klB} \\ -\omega_B Y_{ijB} &= \sum_{kl} P(ij, kl) Y_{klB} + \sum_{kl} R(ij, kl) X_{klB} \end{aligned} \quad (5)$$

P and R are coefficients obtained from the linearization of the commutators $[A(ij), H']$ in RPA manner:

$$[A(ij), H'] = \sum_{kl} P(ij, kl) A(kl) + \sum_{kl} R(ij, kl) A^+(kl)$$

and

$$[A^+(ij), H'] = -\sum_{kl} P(ij, kl) A^+(kl) - \sum_{kl} R(ij, kl) A(kl) \quad (6)$$

The evaluation of P and R are tedious and we quote only the main results. The starting Hamiltonian has the form:

$$\begin{aligned} H &= \sum_i \epsilon_i c_i^+ c_i + 1/2 \sum_{ijkl} V_{ijkl} c_i^+ c_j^+ c_k c_l - \\ &\quad - \sum_{ijm}^{m=\text{occ.}} (V_{imjm} - V_{immj}) c_i^+ c_j \end{aligned} \quad (7)$$

where c_i^+ , (c_i) are creation (annihilation) operators for the i -th molecular orbital level in the Hartree-Fock scheme. For the general Bogoliubov transformation

$$\begin{aligned} c_j &= \sum_i [A_{ij} a_i + B_{ij} a_i^+] \\ c_j^+ &= \sum_i [A_{ij} a_i^+ + B_{ij} a_i] \end{aligned} \quad (8)$$

P and R are

$$\begin{aligned} P(ij, kl) &= T_{ik} - T_{jk} - \sum_{mns} V'_{sns} [(A_{in} A_{km} - B_{im} B_{kn}) - \\ &\quad - (A_{jn} A_{km} - B_{jm} B_{kn})] + 1/2 \sum_{prmn} V'_{prmn} [(A_{ip} A_{jr})' A_{in} A_{km} + \\ &\quad + (B_{in} B_{jm})' B_{lp} B_{kr}] + 1/2 \sum_{rprmn} V'_{rprmn} (A_{ir} B_{jm})' (A_{kn} B_{lp})' \\ R(ij, kl) &= 1/2 \sum_{prmn} V'_{prmn} [(A_{ip} A_{jr})' B_{ln} B_{km} + \\ &\quad + (B_{in} B_{jm})' A_{lp} A_{kr}] + 1/2 \sum_{prmn} V'_{prmn} (A_{jp} B_{im})' (A_{lr} B_{kn})' \end{aligned} \quad (9)$$

with

$$\begin{aligned} (A_{ip}A_{jr})' &= A_{ip}A_{jr} - A_{jp}A_{ir} \\ T_{ik} &= \sum_p \epsilon_p (A_{ip}A_{kp} - B_{ip}B_{kp}) \\ V'_{ijkl} &= V_{ijkl} - V_{ijlk} \end{aligned}$$

With the known expressions for P and R the system of coupled equation (5) can be solved. The resulting coefficients X and Y satisfy orthogonality conditions³. X and Y completely determine the operators Q and Q⁺ and these can be used to find the ground state wave function which is different from the BCS³ ground state wave function:

$$Q_B |\psi_0\rangle = 0 \quad (10)$$

The new ground state wave function $|\psi_0\rangle$ can be easily found. Namely, the following expression is valid:

$$\begin{aligned} |\psi_0\rangle &= |\text{BCS}\rangle + \sum_{ij} b_2 (ij) a_i^+ a_j^+ |\text{BCS}\rangle + \\ &+ \sum_{ijkl} b_4 (ijkl) a_i^+ a_j^+ a_k^+ a_l^+ |\text{BCS}\rangle + \dots \end{aligned} \quad (11)$$

b_2, b_4, \dots are determined using equation (10). It is easy to see that only terms with 0, 4, 8... *quasi*-particles are retained. The excited state wave function is defined as:

$$|\psi_B\rangle = Q_B^+ |\psi_0\rangle \quad (12)$$

From eq. (12) it follows that $|\psi_B\rangle$ contains terms with 2, 6, 10... *quasi*-particles.

More or less as a test we have calculated the transition energies of the molecular systems (ureas) treated previously with the RPA and Hartree-Fock as a ground state wave function. HFB calculation done on these systems did not show any important influence of the pairing interactions. We obtain still lower transition energies in comparison with standard RPA but the lowering is completely negligible (Table I). We conclude that Bogoliubov transformation method has yet to prove its worth by the application to more appropriate molecular systems than the ones studied so far.

TABLE I
Transition Energies (eV)

	RPA	HFB (RPA)
(NH ₂) ₂ CO	6.70	6.69
(NH ₂) ₂ CS	4.93	4.93
(NH ₂) ₂ CSe	4.07	4.05

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IZVLEČEK**Račun eksitacij molekulskega sistema po HFB-SCF metodi v aproksimaciji RPA***B. Lukman in A. Ažman*

Pokazana je uporaba Hartree-Fock-Bogoliubov SCF metodi v Random — Phase-Approximation na določitvi eksitacij molekulskega sistema. Izpeljane so potrebne enačbe in uporabljene pri določitvi energij prehodov sečin.

ODDELEK ZA KEMIJO
UNIVERZA V LJUBLJANI
IN
KEMIJSKI INŠTITUT BORIS KIDRIČ
LJUBLJANA

Sprejeto 21. jula 1969.