

CCA-573

539.19:547.52

Note

Calculation of Collective Modes in π -electron Systems with RPA Method

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Received August 22, 1969

The question of the existence of collective modes in molecular systems is currently attracting much attention both from the theoretical¹ and experimental^{1,2} point of view. In this study we used Random-Phase-Approximation³ to calculate the transition energies and intensities of three π -electron systems: benzene, naphthalene and 1,3,5,7,9-decapentaene. Although it is an oversimplification in the framework of RPA the collective modes are defined as the modes the intensities of which are greatly enhanced in comparison with single transitions.

We applied RPA to relatively small systems for two reasons: *i.* the computational difficulties; *ii.* the instability of the RPA solution when the system exceeds some critical extent⁴.

The system of equations that have to be solved is⁵⁻⁷

$$\begin{aligned} & (e_L - e_v + 2 V_{LvL} - V_{LvLv} - \omega_p) X^{(p)}(L_v) - \\ & \quad - \sum'_{i\alpha} \{ (2 V_{viL\alpha} - V_{vi\alpha L}) X^{(p)}(i\alpha) - \\ & \quad - (2 V_{vaLi} - V_{va\alpha L}) Y^{(p)}(i\alpha) \} = 0 \\ & (e_L - e_v + 2 V_{LvL} - V_{LvLv} + \omega_p) Y^{(p)}(L_v) - \\ & \quad - \sum'_{i\alpha} \{ 2 V_{viL\alpha} - V_{vi\alpha L} \} Y^{(p)}(i\alpha) - \\ & \quad - (2 V_{vaLi} - V_{va\alpha L}) X^{(p)}(i\alpha) \} = 0 \end{aligned}$$

with the notation as in previous paper⁷. The oscillator strengths were calculated from the standard expression for single transitions and from

$$f = 2/3 \omega |D|^2 \quad D = -\sqrt{2} \sum_{i\alpha} [X(i\alpha) + Y(i\alpha)] d_{i\alpha}$$

for RPA.

The starting point of our calculation were the SCF-PPP^{8,9} wave functions. The parametrization for the calculation of the benzene was taken from ref. 10 and for the other two systems the two-center integrals were calculated with the Mataga-Nishimoto prescription. The results are given in Tables I, II, III and IV. The results of the RPA calculation are in good agreement with the extensive calculation done by Pariser¹⁰ and indicate that RPA gives

TABLE I
Benzene Excited States (eV): single transitions and RPA transitions

Single transition		f	RPA	f	
t ₁	5.63	0.11	4.69 (B _{2u})	0	t ₁ , t ₂
t ₂	5.63	0.11	5.84 (B _{1u})	0	t ₃ , t ₄
t ₃	6.22	0.11	6.28 } (E _{1u})	2.4	t ₁ , t ₂ , t ₃ , t ₄
t ₄	6.22	0.11	6.28 }		
t ₅	8.27	0	8.12 } (E _{2g})	0	t ₅ , t ₈
t ₆	8.27	0	8.12 }		
t ₇	8.27	0	8.35 } (E _{2g})	0	t ₆ , t ₈
t ₈	8.27	0	8.35 }		
t ₉	11.34	0	11.28 (B _{1u})	0	t ₉

The last column indicates single transitions largely involved in one particular RPA transition.

TABLE II
Naphthalene Excited States: single transitions and RPA transitions (eV)

Single transition		f	RPA	f	
t ₁	4.69 (B _{2u})	0.38	3.95	0.83	t ₁
t ₂	5.36 (B _{3u})	0.65	4.11	0	t ₂ , t ₃
t ₃	5.36 (B _{3u})	0.65	5.86	1.02	t ₂ , t ₃
t ₄	6.29 (B _{2u})	0.38	6.17	0.36	t ₄

The last column indicates single transitions largely involved in one particular RPA transition.

equivalent results to those of a complete configuration interaction (CI) of single excited states.

This is confirmed by the calculation on naphthalene and 1,3,5,7,9-decapentaene. In naphthalene we did not obtain the correct order of excited states because of the parametrization, but from Table II (the lowest four single transitions are listed) it is evident that RPA gives the results of CI treatment¹⁰. Another example is the mixing of the single excited states of the type ψ_{37} and ψ_{18} with ψ_{26} and ψ_{59} , where (ij) means excitation from the i-th to the j-th molecular orbital. In Table III we quote the eigenfunction X for one particular RPA excitation (8.01 eV). The coefficient gives the weight

TABLE III
Naphthalene: eigenfunction X (each coefficient is labeled by the corresponding ψ_{ij})

X	(ij)
-0.483	26
-0.391	37
0.111	18
-0.297	48
0.715	59

The coefficients not listed are zero.

TABLE IV
 1,3,5,7,9-Decapentaene Excited States: single transitions and RPA transitions (eV)

Single transition	f	RPA	f		
t ₁	5.60	1.03	5.05	1.29	t ₁
t ₂	7.069	~ 0	5.88	~ 0	
t ₃	7.075	~ 0	6.81	8.4.10 ⁻³	t ₅
t ₄	8.05	8.10 ⁻⁴	7.13	~ 0	
t ₅	8.06	8.1.10 ⁻⁴	7.49	~ 0	
t ₆	8.08	0.61	7.56	3.10 ⁻²	t ₄
			8.10	12.10 ⁻⁴	
			8.28	~ 0	
			8.74	0.23	t ₆

The last column indicates single transitions largely involved in one particular RPA transition.

with which ψ_{ij} is involved in a RPA transition. The results obtained with 1,3,5,7,9-decapentaene are similar to the above mentioned ones (Table IV).

In all three molecules studied there are no modes the intensities of which are greatly enhanced in RPA and thus no one has the character of a collective mode. In naphthalene and 1,3,5,7,9-decapentaene the highest RPA transitions are about 1 eV above the single transition with negligible intensities. This confirms the fact that RPA is not suitable for the study of collective modes and improvement has to be introduced into RPA method for the study of these phenomena.

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IZVLEČEK

Račun kolektivnih stanj v π -elektronskih sistemih s RPA metodo

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S RPA metodo so izračunani singletni prehodi in njihove intenzitete v treh π -elektronskih sistemih. Račun pokaže, da s RPA metodo izračunani prehodi nimajo karakterja kolektivnih stanj.

ODDELEK ZA KEMIJO
 UNIVERZE V LJUBLJANI
 IN

KEMIČNI INSTITUT
 »BORIS KIDRIČ«, LJUBLJANA

Priljeno 22. avgusta 1969.