Theoret. Chim. Acta (Berl.) 39, 111—118 (1975)

Commentationes

Random-Phase-Approximation Calculations on Triplet Spectra of Conjugated Molecules

Osamu Matsuoka and Hirotoshi Ito
Department of Physics and Department of Materials Science,
The University of Electro-Communications, Chofu-shi, Tokyo, Japan

Received February 5, 1975

Random-phase approximations (RPA) have been applied to the calculation of the triplet π-π^* transition spectra of 18 conjugated molecules in the framework of Pariser-Parr-Pople approximations. It is found that the normal RPA (n-RPA) shows the triplet instability for most molecules in the Nishimoto-Mataga approximation of electron-repulsion integrals. However, it is shown that this instability can be circumvented by the use of the renormalized RPA (r-RPA) in which the correlated ground states are calculated by the second-order perturbation theory. It is also shown that even in the n-RPA the suitable parametrization of electron-repulsion integrals removes this instability. It is ascertained that such an increasing order of energies as ω(n-RPA) < ω(Tamm-Dancoff approximation) < ω(r-RPA) holds for most of energy levels.

Key words: Random-phase approximation – Triplet instability

1. Introduction

The random-phase approximation (RPA) for calculating electronic spectra has several desirable features. It computes the transition energies directly, it takes into account the correlation effect in its formulation, and the oscillator strengths calculated by the RPA satisfy the Thomas-Kuhn-Reiche sum rule [1].

The RPA [hereafter referred to as normal RPA (n-RPA)] has been employed extensively for calculating spectra of atoms and molecules [2–6]. However, it has often been said [4–6] that one is faced with the difficulty that the lowest (and sometimes even the second lowest) triplet level(s) obtained by the n-RPA turn(s) out to be imaginary. This phenomenon is known as triplet instability [7]. To overcome this difficulty, several improved methods over the n-RPA have been proposed. Shibuya and McKoy [8] and Shibuya *et al.* [9] presented the methods named as higher RPA and renormalized RPA. They [10] applied their methods to N_2, CO, CO_2, water, ethylene, formaldehyde and benzene with successful results. Ostlund and Karplus [11] proposed self-consistent RPA with application to hydrogen molecule. Jørgensen *et al.* [12] presented a modified RPA and self-consistent time-dependent Hartree-Fock method. They applied their methods to some conjugated molecules in the semi-empirical scheme and obtained considerably improved results. All of the methods stated above take into account explicitly the electron correlation effect in the ground (and/or excited) state(s) but differ in their approximations for the matrix elements which appear in the formulations. Terasaka and Matsushita [13] suggested the use of spin-projected Hartree-Fock wave functions in the n-RPA. Jordan [14] applied the several improved methods to ethylene and explained how the triplet instability occurs.

In this note we are especially concerned with the triplet-instability problem in the semi-empirical calculations of conjugated molecules. We have computed the triplet spectra of 18 conjugated molecules by the n-RPA, the renormalized RPA (r-RPA) proposed by Rowe [1] and the Tamm-Dancoff approximation (TDA) in the Pariser-Parr-Pople semi-empirical scheme. The r-RPA was proposed by Rowe [1] for the problem in the nuclear physics and later was employed by Simons [15] for calculating the density matrix of helium atom. The numerical results presented by the previous investigators [10–12, 14, 15] suggest that Rowe's r-RPA is also a simple way to circumvent the triplet instability. Furthermore, both the TDA and the n-RPA are formally derived as the lower order approximations of the r-RPA. Actually, we can describe these three approximations by one formalism [15]. About a decade ago Ball and McLachlan [3] discussed the properties of the n-RPA, where they took ethylene as an example, varied the parameter value appeared in the RPA matrix and showed how the triplet instability occurs. Their work suggest that if the triplet instability arises in the n-RPA we can avoid that instability by varying the parameter values appearing in the calculation. Therefore, in our computations we have employed several currently proposed approximations of the electron-repulsion integrals and compared the calculated results. We have done the TDA calculations only for comparative purpose, for the TDA is actually known to be the configuration-interaction method with single excitations [1] which has been usually employed in the semi-empirical calculations.

The results obtained show that we can circumvent the triplet instability in the n-RPA by going up to the higher-order approximations such as the r-RPA or by adopting the suitable parametrization within the n-RPA.

2. Calculation of Triplet Spectra

The general form of RPA equation given by Rowe [1] is

$$\begin{bmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ -\tilde{\boldsymbol{B}}^{+} & -\tilde{\boldsymbol{A}}^{*} \end{bmatrix} \begin{bmatrix} \tilde{\boldsymbol{Y}} \\ \tilde{\boldsymbol{Z}} \end{bmatrix} = \omega_\lambda \begin{bmatrix} \tilde{\boldsymbol{Y}} \\ \tilde{\boldsymbol{Z}} \end{bmatrix},$$

where ω_λ is the transition energy from ground state to excited state λ, and $\tilde{\boldsymbol{Y}}$ and $\tilde{\boldsymbol{Z}}$ are the coefficients of one-electron excitation and deexcitation operators appearing in the usual RPA operator. The expressions of matrix elements $\tilde{\boldsymbol{A}}$ and $\tilde{\boldsymbol{B}}$ are given in Eq. (2.28) in Ref. [15]. The n-RPA arises if we take the ground state as the Hartree-Fock ground state and if we further put the coefficient $\tilde{\boldsymbol{Z}}$ as zero, we obtain the TDA. The r-RPA results if we introduce the correlation effect into the ground state.

We have applied the TDA, the n-RPA, and the r-RPA to 18 conjugated molecules. The Hartree-Fock molecular orbitals are obtained in the Pariser-Parr-Pople approximation. Parameter values used for ionization potentials and

Table 1. Resonance integrals and bond distances

		Resonance integral (eV)	Bond distance (Å)
Ethylene	C=C	−2.92	1.35
Formaldehyde	C=O	−2.692	1.21
Butadiene[a]	C=C	−2.92	1.35
	C–C	−1.16	1.46
Glyoxal	C=O	−2.50	1.20
	C–C	−1.16	1.46
Para-benzoquinone	C=O	−2.692	1.23
	C–C	−2.39	1.27
	C=C	−2.39	1.32
Other molecules	CC (Ring)	−2.39	1.39
	CN (Ring)	−2.576	1.39
	C–OH	−2.50	1.36
	$C-NH_2$	−2.50	1.38

[a] $<C_1C_2C_3=124°$.

one-center electron-repulsion integrals γ_{pp} are those adopted by Bailey [16] (the set B in Table 1, [16]). The parametrizations gave a satisfactory agreement with experimental values of singlet absorption spectra of benzene-like heterocyclic compounds [16]. Two-center electron-repulsion integrals γ_{pq} are calculated by the Nishimoto-Mataga's formula [17] (N-M): $(R_{pq}+a_{pq})^{-1}$, the Ohno's formula [18]: $(R_{pq}^2+a_{pq}^2)^{-1/2}$, the Chojnacki's formula [19]: (0.4 N-M+0.6 Ohno), and a new formula: $(R_{pq}^3+a_{pq}^3)^{-1/3}$, where R_{pq} is the distance between atoms p and q and $a_{pq}=2/(\gamma_{pp}+\gamma_{qq})$. The formula proposed here is apparently similar to the N-M's and the Ohno's formulas. We also use the Pariser's quadratically interpolated formula [20] in which effective nuclear charges are calculated by Slater's rule. Resonance integrals and bond distances used in the calculations are assumed, or taken from various references. They are shown in Table 1. A regular hexagon is assumed for benzene rings. Azulene and aza-azulene are assumed to be a regular pentagon plus a heptagon.

All the singly excited configurations are taken into account in the RPA excitation-deexcitation operator. In the r-RPA the charge densities of correlated ground state are evaluated using the second-order Rayleigh-Schrödinger perturbation theory in which only doubly excited configurations are considered. We have not done the iterative process adopted by Shibuya and McKoy [8] to obtain the charge densities of the correlated ground states, for the iterative process does not seem to be essential for introducing further correlation effect into the ground state. In fact, the results obtained by perturbation theory are known to be close to the iterative ones [8, 9].

3. Results and Discussion

In Table 2, we summarize the comparison of the energies of the lowest and/or the second lowest triplet levels of conjugated molecules calculated by several approximations of the repulsion integrals γ_{pq} in the n-RPA, the TDA, and the

Table 2. Comparison of triplet π-π^* transition energies

	Nishimoto-Mataga			Chojnacki			Ohno			Proposed			Pariser			Obs.
	n-RPA	TDA	r-RPA	n-RPA	TDA	r-RPA	n-RPA	TDA	r-RPA	n-RPA	TDA	r-RPA	n-RPA	TDA	r-RPA	
Ethylene																
B_{3u}	0.40	2.94	3.00	2.96	3.67	3.76	3.75	4.12	4.21	4.42	4.59	4.66	3.71	4.10	4.19	4.6 [4]
Formaldehyde																
A_1	Im.	2.37	2.04	2.38	3.26	3.23	3.46	3.87	3.90	4.35	4.53	4.56	3.43	3.85	3.88	
Trans-butadiene																
B_u	Im.	2.19	1.62	1.15	2.72	2.52	2.23	3.07	3.01	2.93	3.43	3.46	2.39	3.15	3.09	2.56 [21]
Cis-butadiene																
B_2	Im.	2.19	1.64	1.17	2.72	2.54	2.24	3.07	3.00	2.93	3.43	3.48	2.40	3.15	3.10	
Glyoxal																
B_u	Im.	2.10	1.94	1.95	3.00	2.73	3.09	3.56	3.47	3.95	4.15	4.13	3.15	3.60	3.52	
A_u	Im.	2.49	1.24	2.45	3.29	3.14	3.46	3.85	3.81	4.25	4.43	4.43	3.53	3.91	3.87	
Benzene																
B_{1u}	Im.	2.50	1.72	1.95	3.06	2.89	2.78	3.44	3.52	3.42	3.82	4.17	2.81	3.43	3.47	3.95 [22]
E_{1u}	3.93	4.01	4.47	4.26	4.29	4.76	4.47	4.48	4.98	4.70	4.70	5.30	4.40	4.42	4.87	4.75
B_{2u}	4.85	4.91	5.30	4.85	4.95	5.31	4.84	4.98	5.34	4.82	5.02	5.44	4.81	4.91	5.26	5.60
E_{2g}	5.23	5.49	5.77	5.91	6.02	6.31	6.32	6.37	6.69	6.75	6.76	7.14	6.26	6.32	6.59	6.75
	8.52	8.52	8.79	8.98	8.98	9.22	9.29	9.29	9.52	9.73	9.74	9.99	9.03	9.03	9.25	8.9
B_{1u}	10.58	10.62	10.77	11.27	11.29	11.38	11.73	11.73	11.79	12.36	12.36	12.39	11.41	11.41	11.48	
Pyridine																
A_1	Im.	2.64	1.92	2.21	3.27	3.07	3.04	3.04	3.73	3.81	4.13	4.45	3.03	3.61	3.66	3.68 [23]
Pyrimidine																
A_1	Im.	2.85	2.16	2.66	3.52	3.36	3.56	4.03	4.10	4.46	4.54	4.91	3.46	3.94	3.98	3.51 [23]

Pyrazine																
B_{2u}	Im.	2.77	2.03	2.24	3.27	3.13	3.33	3.48	3.75	3.30	3.49	4.02	3.06	3.64	3.71	3.29 [23]
s-Triazine																
A_1	1.23	3.14	2.50	3.26	3.97	3.81	4.28	4.66	4.69	5.55	5.71	5.86	4.09	4.49	4.49	
Aniline																
A_1	Im.	2.30	1.46	1.94	3.05	2.87	2.76	3.41	3.50	3.39	3.79	4.13	2.78	3.41	3.46	3.32 [21]
Phenol																
A_1	Im.	2.40	1.58	1.94	3.05	2.87	2.76	3.42	3.50	3.40	3.80	4.14	2.78	3.41	3.45	3.54 [21]
Para-benzoquinone																
B_{2u}	Im.	0.49	Im.	Im.	1.11	0.56	Im.	1.55	1.45	1.24	2.04	2.08	Im.	1.45	1.45	
B_{1g}	Im.	1.47	1.83	1.15	1.96	2.32	1.90	2.32	2.65	2.56	2.76	3.06	1.78	3.51	2.63	
Naphthalene																
B_{2u}	Im.	1.71	Im.	0.51	2.16	1.64	1.69	2.47	2.28	2.33	2.79	2.86	1.69	2.44	2.25	2.63 [21]
Quinoxaline																
B_2	Im.	1.69	Im.	0.76	2.24	1.40	1.80	2.54	2.18	2.96	3.16	3.35	1.81	2.52	2.15	2.65 [21]
Azulene																
A_1	Im.	1.39	Im.	Im.	1.77	0.29	0.79	2.04	1.44	1.68	2.35	2.09	2.12	2.42	2.39	
B_2	1.40	1.47	1.62	1.51	1.60	1.75	1.59	1.72	1.85	1.72	1.92	2.20	1.67	1.71	1.93	
A_1	2.19	2.31	2.45	2.39	2.47	2.65	2.51	2.58	2.79	2.65	2.73	3.00	3.60	3.66	3.81	
1,3-Diazaazulene																
A_1	Im.	1.64	Im.	Im.	1.98	0.86	1.13	2.19	1.81	1.71	2.36	2.11	1.18	2.19	1.83	
Anthracene																
B_{2u}	Im.	1.00	Im.	Im.	1.38	Im.	Im.	1.64	0.25	1.23	1.91	1.30	Im.	1.60	0.16	1.85 [21]
B_{2u}	Im.	2.15	Im.	1.81	2.57	1.90	2.40	2.85	2.47	2.88	3.15	2.94	3.29	3.55	3.33	

r-RPA. In the n-RPA done by the N-M formula, most of molecules are found to obtain imaginary energies for the lowest triplet levels. It is further noticed that glyoxal, para-benzoquinone, azulene, and anthracene have imaginary energies even in the second lowest triplet levels. From Table 2, it is seen that this difficulty of the triplet levels in the n-RPA is considerably improved in Chojnacki's and Ohno's approximations except for para-benzoquinone, azulene, 1,3-diazaazulene, and anthracene which are, however, shown to attain real energies in the second lowest levels. This observation is almost true for the results obtained by Pariser's formula in which the imaginary energies are seen only in the lowest triplet levels of parabenzoquinone and anthracene in the n-RPA. In the approximation proposed here, the imaginary energies for the lowest triplet levels are not found any more in the molecules treated in this work. This approximation gives the best n-RPA results in agreement with the observed values [4, 21–23].

In the r-RPA, the triplet instability does not occur except for the N-M approximation where the difficulty can be overcome for small molecules but still remains for large molecules. In the r-RPA Pariser's formula seems to give the best results comparing to the experimental values [4, 21–23].

From Table 2, it is seen that the relationship of energy levels such as $\omega(\text{n-RPA}) < \omega(\text{TDA}) < \omega(\text{r-RPA})$, which has been proved by Ostlund and Karplus [11] for two-electron system, holds for the most molecules. It can be ascertained from Table 2 that $\omega(\text{n-RPA}) < \omega(\text{TDA})$ holds for any approximations of electron repulsion integrals employed, whereas $\omega(\text{TDA}) < \omega(\text{r-RPA})$ is not always found to be true. The reversed inequalities such as $\omega(\text{TDA}) > \omega(\text{r-RPA})$ are seen when the triplet instability in the n-RPA occurs.

In the case of ethylene molecule, we can see more clearly the parameter dependence of the transition energies. Following the arguments by Ball and McLachlan [3], we can write the triplet transition energies as

$$\begin{aligned}
\omega(\text{TDA}) &= -g-2\beta \\
\omega(\text{n-RPA}) &= 2[-\beta(-g-\beta)]^{1/2} \\
\omega(\text{r-RPA}) &= 2[-\beta+2^{-1}(1-x)\gamma_{ab}]^{1/2}[-xg-\beta+2^{-1}(1-x)\gamma_{ab}]^{1/2},
\end{aligned}$$

where

$$\begin{aligned}
g &= 2^{-1}(\gamma_{aa}-\gamma_{ab}) \\
x &= 2^{-1}(\varrho_1-\varrho_2).
\end{aligned}$$

In the above equations β is the resonance integral between carbon atoms a and b. ϱ_1 and ϱ_2 are charge densities in the lowest and the second lowest molecular orbitals. The x in the above equations comes to be $0.89 \sim 0.98$ for the approximations of electron-repulsion integrals adopted here. Assuming $x=0.89$ we have Fig. 1 for the transition energies. It is seen in Fig. 1 that the triplet energy obtained by the n-RPA is a monotonic decreasing function of the parameter g and that the energy calculated by the N-M approximation is about to vanish. This indicates the incipient triplet instability in the N-M approximation. These instabilities are not seen in other approximations of electron-repulsion integrals and in the TDA and the r-RPA.

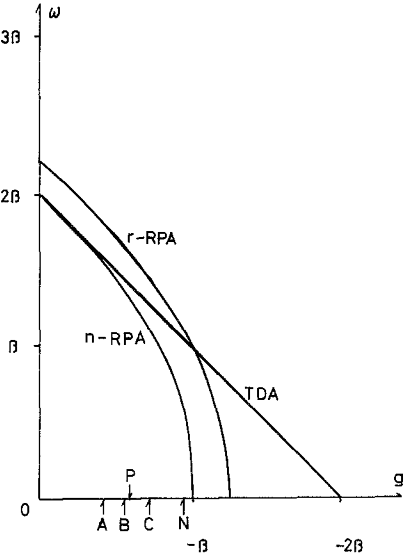

Fig. 1. Dependence of RPA triplet transition energies of ethylene on approximations of electron-repulsion integrals. The arrows on the abscissa indicates the values of parameter g in the approximation of integrals (A: Proposed, B: Ohno, C: Chojnacki, P: Pariser, N: Nishinoto-Mataga. See text)

The computations presented here show that we can avoid the triplet instability in the n-RPA by using proper parametrization of integrals or by adopting the higher-order approximations of the n-RPA such as the r-RPA. In other words, the deficiency of the n-RPA can be overcome to some extent by introducing the electron correlation effect, one of ways being (probably) the parametrization or the use of the r-RPA. For large molecules on which the *ab initio* calculations are difficult, the semi-empirical treatment is one of ways for solving the problem. In that treatment of RPA, it seems hopeful to use proper parametrizations as we have done here.

References

1. Rowe, D. J.: Rev. Mod. Phys. **40**, 153 (1968)
2. Altick, P. L., Glassgold, A. E.: Phys. Rev. **3**A, 632 (1964);
   Dunning, T. H., McKoy, V.: J. Chem. Phys. **48**, 5263 (1968);
   Guifreund, H., Little, W. A.: Phys. Rev. **183**, 68 (1969);
   Guifreund, H., Little, W. A.: J. Chem. Phys. **50**, 4468 (1969); J. Chem. Phys. **50**, 4478 (1969);
   Jørgensen, P.: J. Chem. Phys. **56**, 1839 (1972);
   Kitaura, K., Nishimoto, K.: Theoret. Chim. Acta (Berl.) **28**, 111 (1973);
   Tanaka, M., Tanaka, J.: Theoret. Chim. Acta (Berl.) **30**, 81 (1973)
3. Ball, M. A., McLachlan, A. D.: Mol. Phys. **7**, 501 (1964)
4. Dunning, T. H., McKoy, V.: J. Chem. Phys. **47**, 1735 (1967)
5. Jørgensen, P., Linderberg, J.: Intern. J. Quantum Chem. **4**, 587 (1970)
6. Ho, J. C., Segal, G. A., Taylor, H. S.: J. Chem. Phys. **56**, 1520 (1972)
7. Cizek, J., Paldus, J.: J. Chem. Phys. **47**, 3976 (1967)
8. Shibuya, T., McKoy, V.: Phys. Rev. A**2**, 2208 (1970)
9. Shibuya, T., Rose, J., McKoy, V.: J. Chem. Phys. **58**, 500 (1973)

10. Shibuya, T., McKoy, V.: J. Chem. Phys. **53**, 3308 (1970); J. Chem. Phys. **54**, 1738 (1971); Conghran, W., Rose, J., Shibuya, T., McKoy, V.: J. Chem. Phys. **58**, 2699 (1973); Rose, J., Shibuya, T., McKoy, V.: J. Chem. Phys. **60**, 2700 (1974); Yeargen, D. L., McKoy, V.: J. Chem. Phys. **60**, 2714 (1974); Yeargen, D. L., McKoy, V., Segal, G. A.: J. Chem. Phys. **61**, 755 (1974); McCurdy, C. W., McKoy, V.: J. Chem. Phys. **61**, 2820 (1974)
11. Ostlund, N., Karplus, M.: Chem. Phys. Letters **11**, 450 (1971)
12. Linderberg, J., Jørgensen, P., Oddershede, J., Ratner, M.: J. Chem. Phys. **56**, 6213 (1972); Linderberg, J., Jørgensen, P., Oddershede, J.: J. Chem. Phys. **57**, 277 (1972); Jørgensen, P., Oddershede, J., Ratner, M.: J. Chem. Phys. **61**, 710 (1974)
13. Terasaka, T., Matsushita, T.: Chem. Phys. Letters **4**, 384 (1969)
14. Jordan, K. D.: Intern. J. Quantum Chem. **7**, 491 (1973)
15. Simons, J.: J. Chem. Phys. **55**, 1218 (1971)
16. Bailey, M. L.: Theoret. Chim. Acta (Berl.) **13**, 56 (1969)
17. Mataga, N., Nishimoto, K.: Z. Physik. Chem. **13**, 140 (1957)
18. Ohno, K.: Theoret. Chim. Acta (Berl.) **2**, 219 (1964)
19. Chojnacki, H.: Theoret. Chim. Acta (Berl.) **11**, 174 (1968)
20. Pariser, R.: J. Chem. Phys. **24**, 324 (1956)
21. McGlynn, S. P., Azumi, T., Kinoshita, M.: Molecular spectroscopy of triplet state. New York Prentice-Hall 1969
22. Karkowski, J.: Acta Phys. Polon. A**37**, 417 (1970)
23. Goodman, L.: J. Mol. Spectry. **6**, 109 (1961)

Dr. Osamu Matsuoka
Department of Physics
The University of Electro-Communications
Chofu-shi, Tokyo, Japan