Theoret. Chim. Acta (Berl.) 49, 151–160 (1978)

THEORETICA CHIMICA ACTA

Screened Potential in π-Electron Systems and Its Application to the Estimation of Excitation Energies

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A diagrammatic technique was developed for the estimation of the screened potential of π-electron systems. The screened potential was expanded in terms of the polarization propagators which were constructed from either the singlet, $\hat{\Gamma}^1$, or triplet vertex part, $\hat{\Gamma}^3$. These vertex parts correspond to the singlet or triplet excitations, respectively, in the Random Phase Approximation (RPA) containing exchange diagrams. The excitation energies were calculated by using the screened potential in the framework of RPA with exchange. The excitation energies of several conjugated molecules with or without a hetero atom are in agreement with the experimental data.

Key words: Screened potential – Green's function – π-Electron systems, excitation energies of ~

1. Introduction

The excitation energies of a molecule are quantities of extreme importance in considering the electronic states of the molecule. They can be determined directly by use of the RPA method without the knowledge of the energies of the individual states involved in the excitation process [1–4]. However, the RPA method has a defect that the lowest triplet excitation energies calculated by this method turn out to be imaginary. Shibuya and McKoy have introduced the higher RPA method to remove this defect [5].

A previous paper [6] showed that the parameters based on Löwdin's orthogonal orbitals gave the triplet instability, even if the Green's function involving second-order perturbation terms was employed. On the other hand, the excitation energies calculated by the semi-empirical parameters agreed well with the experimental values, even when only the first-order perturbation terms were taken

0040-5744/78/0049/0151/$02.00

into account [6]. These results indicate that the effect due to the electron repulsion integrals is most important in the evaluation of the excitation energies, and that the excitation energies will be improved by considering the effective interaction including the correlation effect.

Gutfreund and Little [7] constructed the effective interaction by summing up both the lowest ring diagrams and the diagonal parts of oysters, and calculated the excitation energies of π-electron systems in the framework of the configuration interaction method. Tanimoto and co-workers [8] presented another type of the effective interaction by using the ladder diagrams, and discussed the correlation energies.

Cooper and Linderberg [9] applied the Coulomb hole and screened exchange approximation, which was developed by Hedin [10], to the Pariser–Parr–Pople (PPP) method [11]. In their treatment, 1) the PPP parameters were used as the bare potential, and 2) the atom-atom polarizabilities, π_{tu}, were expressed in terms of the triplet vertex, $\Gamma^3_{rs,t}$, which corresponds to the triplet excitation in the static case, and they were summed up into the effective interaction instead of the lowest ring diagram. We regard that the PPP parameters are not appropriate as the bare potential, since they contain inherently the screening effect. Moreover, the contribution of the singlet vertex, $\Gamma^1_{rs,t}$, to the excitation energies has not been examined.

In this paper, the values of the bare potential are calculated theoretically by means of the Slater type orbitals [13], and the effective interaction, which involves either the singlet vertex, $\Gamma^1_{rs,t}$, or the triplet vertex, $\Gamma^3_{rs,t}$, is derived by using diagrammatic techniques. The RPA with exchange, or equivalently the time dependent Hartree–Fock (TDHF) method will be applied to the estimation of the excitation energies. The evaluation of the matrix element is also discussed.

2. Theory

2.1. One-Particle Green's Function [15, 16]

The one-particle Green's function matrix in the ω representation can be written as

$$\hat{G}(\omega)=[\hat{G}^{0^{-1}}(\omega)-\hat{\Sigma}(\omega)]^{-1}, \tag{1}$$

where $\hat{G}^0(\omega)$ is the Green's function matrix for an unperturbed system, $\hat{\Sigma}(\omega)$, the perturbation matrix termed self-energy. If one chooses a Hückel-type Hamiltonian, $\hat{H}_0$, as the unperturbed one and the first-order self-energy, $\hat{\Sigma}^{(1)}$, as $\hat{\Sigma}(\omega)$, then

$$\begin{aligned}\hat{G}(\omega)&=[\hat{G}^{0^{-1}}(\omega)-\hat{\Sigma}^{(1)}]^{-1}\\&=[\omega\hat{I}-(\hat{H}_0+\hat{\Sigma}^{(1)})]^{-1}\\&=[\omega\hat{I}-\hat{F}]^{-1},\end{aligned} \tag{2}$$

where $\hat{F}$ is the Fock operator. If the Fock operator is evaluated by the PPP approximation, the matrix elements of the Green's function, $\hat{G}(\omega)$, become

$$G_{kl}(\omega) = \sum_{i}^{\text{occ}} \frac{C_{ki}C_{li}}{\omega - \omega_i - i\delta} + \sum_{i}^{\text{unocc}} \frac{C_{ki}C_{li}}{\omega - \omega_i + i\delta}, \tag{3}$$

where ω_i's are the eigenvalues of $\hat{F}$ and C_i are the corresponding eigenvectors. The matrix elements of the electronic interaction are approximated by the following form;

$$\begin{aligned} V^{\eta\eta'}_{pr;sq} &= \iint dr_1\, dr_2 \phi^*_{p\eta}(r_1)\phi^*_{r\eta'}(r_2)V(|r_1 - r_2|)\phi_{s\eta'}(r_2)\phi_{q\eta}(r_1) \\ &= \gamma_{pr}(1 - \delta_{\eta\eta'}\,\delta_{pr})\,\delta_{pq}\,\delta_{rs}, \end{aligned} \tag{4}$$

where ϕ_p is the p'th atomic orbital and η denotes the spin function. The first-order irreducible self-energies are shown diagrammatically in Fig. 1. The diagram (a) is evaluated from the Feynman–Dyson rule by

$$\Sigma^{(1)}_{ll} = \sum_{i}^{\text{occ}} \left(C_{li}C_{li}\gamma_{ll} + \sum_{p(\neq l)} 2C_{pi}C_{pi}\gamma_{lp} \right), \tag{5a}$$

and the diagram (b) is also evaluated by

$$\Sigma^{(1)}_{lm} = -\gamma_{lm} \sum_{i}^{\text{occ}} C_{li}C_{mi}, \quad (l \neq m). \tag{5b}$$

Note that the diagram (a) represents the diagonal elements of the HF potential and the diagram (b) the off-diagonal ones. The Green's function matrix can be obtained by an iteration method which is discussed in the following section.

2.2. *Screened Potential*

The screened potential [7, 9] is written as

$$\tilde{\gamma}_{rs} = \gamma_{rs} + \sum_{tu} \tilde{\gamma}_{rt}\pi_{tu}\gamma_{us}, \tag{6}$$

and its matrix form becomes

$$\hat{\tilde{\gamma}} = [\hat{\gamma}^{-1} - \hat{\pi}]^{-1}, \tag{7}$$

where γ_{rs} is the bare potential and π_{tu} represents the atom-atom polarizability. If one multiplies the polarization propagator by the factor 2 and puts the frequency, ω, to be zero, then the resultant becomes the atom-atom polarizability, π_{tu} [12]. This static screening case is treated. Eq. (6) is shown diagrammatically in Fig. 2(a).

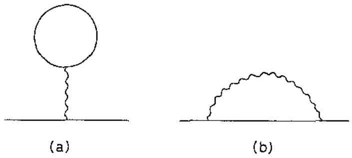


Fig. 1. First-order irreducible diagrams

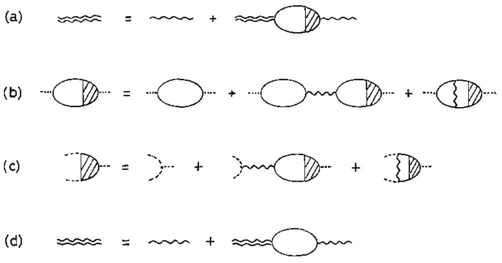


Fig. 2. (a) Diagrammatic representation of Eq. (6). (b) Dyson equation for the polarization propagator. (c) Equation for the vertex part of the polarization propagator. (d) Gutfreund and Little's screened potential [7]

From this diagram, π_{tu} is constructed by the free propagated part, $\pi^0_{uu;rs}$, and by the vertex part, $\Gamma_{rs,t}$, and is written as

$$\begin{aligned}\pi_{tu} &= \sum_{rs} \pi^0_{uu;rs} \Gamma_{rs,t} \\ &= \sum_{rs} \pi^0_{u;rs} \Gamma_{rs,t},\end{aligned} \tag{8}$$

$$\pi^0_{uv;rs} = (\pi i)^{-1} \int d\omega G_{ur}(\omega) G_{sv}(\omega). \tag{9}$$

The polarization propagator in the RPA with exchange is represented diagrammatically in Fig. 2(b), and the vertex part in Fig. 2(c).

The vertex parts for both the triplet and the singlet excitations are given by

$$\hat{\Gamma}^3 = \hat{\Gamma}^{\eta\eta} - \hat{\Gamma}^{\eta-\eta}, \tag{10a}$$

and

$$\hat{\Gamma}^1 = \hat{\Gamma}^{\eta\eta} + \hat{\Gamma}^{\eta-\eta}, \tag{10b}$$

respectively [17]. The triplet and the singlet vertices, $\Gamma^3_{rs,t}$ and $\Gamma^1_{rs,t}$, are derived from Fig. 2(c) and Eqs. (10a), (10b);

$$\Gamma^3_{rs,t} = \delta_{rt}\,\delta_{st} - \tfrac{1}{2}\tilde{\gamma}_{rs} \sum_{uv} \pi^0_{rs;uv} \Gamma^3_{uv,t}, \tag{11a}$$

$$\Gamma^1_{rs,t} = \delta_{rt}\,\delta_{st} - \tfrac{1}{2}\tilde{\gamma}_{rs} \sum_{uv} \pi^0_{rs;uv} \Gamma^1_{uv,t} + \tfrac{1}{2}\tilde{\gamma}_{rs} \sum_{uv} (\pi^0_{rr;uv} + \pi^0_{ss;uv}) \Gamma^1_{uv,t}, \tag{11b}$$

where the bare potential, γ_{rs}, in Fig. 2(b) is replaced by the screened potential, $\tilde{\gamma}_{rs}$. If one neglects the second or higher terms in Eqs. (11a) and (11b), they become Gutfreund and Little's equations, and are shown in Fig. 2(d).

We propose the following steps for practical computation: Step 1: Calculate the Green's function, $\hat{G}(\omega)$, by using the bare potential for the Fock operator, and obtain the values of $\pi^0_{uv;rs}$ in Eq. (9).
Step 2: Choose the first term of Eqs. (11a), (11b) as the initial $\Gamma^{3(1)}_{rs,t}$, and obtain π_{tu} from Eq. (8).
Step 3: Calculate the screened potential, $\tilde{\gamma}_{rs}$, in Eq. (7), and construct the new Green's function, $\hat{G}(\omega)$, by using the $\tilde{\gamma}_{rs}$.
Step 4: Replace the vertex, $\Gamma^{3(1)}_{rs,t}$, in the right hand side of Eqs. (11a), (11b) with the previous ones.

Compare the screened potential, $\tilde{\gamma}_{rs}$, with that obtained in the iteration process just before and this procedure is repeated until the self-consistency in the screened potential is achieved. Note that the bare potential must be always inserted into γ_{rs} in Eq. (5a). Since our interest is to estimate the correlation between the interacting electrons, the matrix elements of the one-particle operator are of less importance. They are obtained from Ref. [11].

2.3. Excitation Energies

The excitation energies are calculated in the framework of RPA with exchange by using the screened potential which was calculated in the previous section. The complete details are given by Jørgensen and Linderberg [14]. The equation to be solved is

$$\det \begin{vmatrix} \hat{A} & \hat{B} \\ -\hat{B} & -\hat{A} \end{vmatrix} = 0, \tag{12}$$

where the matrix elements are

$$A^{s}_{i\alpha;\, j\beta} = \delta_{ij}\,\delta_{\alpha\beta}(\omega_\alpha - \omega_i) + 2(i\alpha \mid j\beta) - (ij \mid \alpha\beta), \tag{13a}$$

$$B^{s}_{i\alpha;\, j\beta} = 2(i\alpha \mid j\beta) - (i\beta \mid j\alpha), \tag{13b}$$

$$A^{t}_{i\alpha;\, j\beta} = \delta_{ij}\,\delta_{\alpha\beta}(\omega_\alpha - \omega_i) - (ij \mid \alpha\beta), \tag{14a}$$

$$B^{t}_{i\alpha;\, j\beta} = -(i\beta \mid j\alpha), \tag{14b}$$

and

$$(ij \mid kl) = \sum_{pq} C_{pi}\, C_{pj}\, C_{qk}\, C_{ql}\, \gamma_{pq}\,. \tag{15}$$

Here s refers to a singlet excitation and t to a triplet excitation, and i, j are in connection with occupied orbitals in the ground state and α, β with unoccupied ones.

3. Results and Discussion

3.1. Benzene

The bare and screened potentials, together with the PPP parameters, and the orbital energies for benzene are given in Table 1. The bare potentials were calculated from Slater orbitals with $Z = 3.25$. The screening effect makes the one-center electron repulsion integral, γ_{11}, small, and hence $\tilde{\gamma}_{11}$ has its value close to the one of the PPP parameters. This means that the PPP parameters inherently involve the effect of electron correlation. It is interesting that $\tilde{\gamma}_{14}$ is considerably larger than γ_{14}. This tendency was observed in the other molecules.

Using these potentials, the excitation energies of benzene were calculated. They are listed in Table 2. The calculation with the bare potential gave an imaginary value for the lowest triplet excitation energy. The PPP parameters gave rise to an

Table 1. Bare and screened potential values and orbital energies for benzene (in eV)

	Bare[a]	PPP[b]	$\hat{\Gamma}^3$ Screened[c]	$\hat{\Gamma}^1$ Screened[d]
γ_{11}	17.31	11.35	11.51	12.81
γ_{12}	9.06	7.19	8.76	8.89
γ_{13}	5.67	5.77	7.50	7.07
γ_{14}	4.96	4.97	7.72	7.10
Orbital energies	−10.57	−8.71	−9.90	−10.10
	−6.53	−5.60	−6.88	−6.83

[a] Calculated with Slater orbitals, $Z=3.25$, C–C 1.397 Å.

[b] Given by Parr [11].

[c] Calculated from Eq. (11a), $\beta=-2.68$, $I_p=11.16$.

[d] Calculated from Eq. (11b).

Table 2. Excitation energies for benzene in various potentials (in eV)

			$\hat{\Gamma}^3$ Screened		$\hat{\Gamma}^1$ Screened		
	Bare	PPP	$2(i\alpha \mid j\beta)$ Bare[a]	All screened[b]	$2(i\alpha \mid j\beta)$ Bare	All screened	Exp.
$^1B_{2u}^-$	5.43	4.66	5.60	5.47	5.62	5.56	4.89[18]
$^1B_{1u}^+$	6.88	5.88	7.58	5.60	7.63	5.62	6.17
$^1E_{1u}^+$	8.66	6.44	8.99	6.66	9.02	7.23	6.98
$^1E_{2g}^+$	10.51	8.13	9.09	8.99	9.57	9.57	
$^1E_{2g}^-$	11.09	8.56	11.58	9.23	11.38	9.57	
$^1B_{1u}^+$	14.47	11.50	13.01	11.67	13.29	12.36	
$^3B_{1u}^+$	—	2.21	4.23		3.41		3.95[19]
$^3E_{1u}^+$	4.33	4.11	5.13		5.02		4.75
$^3B_{2u}^-$	5.43	4.66	5.60		5.62		5.60
$^3E_{2g}^+$	5.43	5.85	7.29		6.97		6.75
$^3E_{2g}^-$	11.09	8.56	8.99		9.57		8.9
$^3B_{1u}^+$	13.79	10.82	11.37		11.98		

[a] The term $2(i\alpha \mid j\beta)$ in Eqs. (13a), (13b) is evaluated by substituting the bare potential for the screened potential. In the case of the triplet excitations, the matrix elements contain no such term, so that the values of excitation energies are equal to those of the case in which all terms in Eqs. (14a), (14b) are evaluated by use of the screened potential.

[b] All terms in Eqs. (13a), (13b) are evaluated by use of the screened potential.

apparent deviation from the experimental value for the lowest $^3B_{1u}^+$ state. The use of the screened potential, however, gave better results (Table 2). Since the total energy of the ground state was only 1 eV lower than that obtained from the bare potential, the improvement of the ground state energy may not be sufficient for the evaluation of the excitation energies.

Table 3. Bare and screened potentials for butadiene (in eV)

	Bare[a]	PPP[b]	$\hat{\Gamma}^3$ Screened	$\hat{\Gamma}^1$ Screened
γ_{11}	17.31	11.35	12.77	13.42
γ_{12}	9.33	7.19	11.56	11.07
γ_{13}	5.57	5.77	6.48	6.36
γ_{14}	3.81	4.00	6.60	6.29
γ_{22}	17.31	11.35	13.56	14.17
γ_{23}	8.72	7.19	6.87	7.34

[a] $Z=3.25$, C_1–C_2 1.343 Å, C_2–C_3 1.467 Å, $\sphericalangle C_1$–C_2–C_3 122.8°. These experimental values are taken from [20].

[b] Given by Parr [11].

3.2. *Trans-Butadiene and trans-Hexatriene*

The bare and screened potentials of butadiene are listed in Table 3. The screened potential $\tilde{\gamma}_{11}$ is smaller than $\tilde{\gamma}_{22}$. Semi-empirical methods, in which the potentials are calculated from the function of two atomic distances, cannot describe this correlation effect. The excitation energies of butadiene are given in Table 4. Cooper and Linderberg pointed out that the use of bare potential for $2(i\alpha \mid j\beta)$ removes the over-estimation of the screening effect in a diagrammatic expansion [9]. However, this method gave poor excitation energies of butadiene and hexatriene (Table 4).

Various potentials in hexatriene are illustrated in Fig. 3. It was found that when the distance between interacting electrons is shorter than the nuclear distances, the screened potential strongly differs from the bare potential. In this region, the bare potential is local and varies very rapidly with the distance between the interacting electrons, while the screened potential is nonlocal, slowly varies and is quite suitable for a HF calculation. For large distances, the screened potentials become wavy, because the effective interactions are expanded by particle-hole propagators which are applicable to the electron gas. The same tendency appeared in the application of Little's method to conjugated polyenes [22]. Table 5 presents several lowest excitation energies of hexatriene.

Table 4. Excitation energies for butadiene (in eV)

			$\hat{\Gamma}^3$ Screened		$\hat{\Gamma}^1$ Screened		
	Bare	PPP	$2(i\alpha \mid j\beta)$ Bare	All screened	$2(i\alpha \mid j\beta)$ Bare	All screened	Exp.[21]
1_{B_u}	6.55	4.89	8.34	5.01	7.99	5.26	5.92
	11.68	9.26	13.14	12.25	12.78	11.94	
1_{A_g}	8.89	6.48	10.34	6.61	9.88	7.19	
	9.03	6.60	10.69	10.34	10.42	9.88	
3_{B_u}	—	—	3.73		2.97		3.22
	9.58	7.68	11.36		10.85		
3_{A_g}	—	2.86	4.81		4.35		4.91
	8.89	6.48	10.34		9.88		

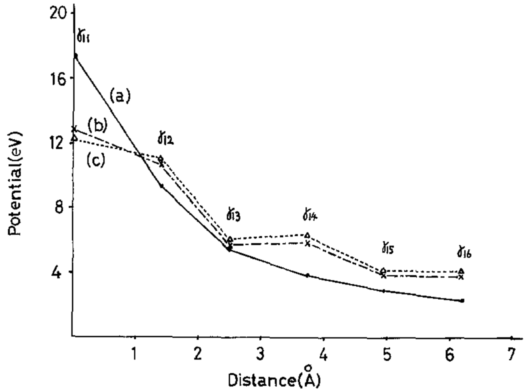


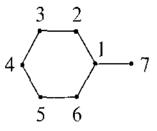
Fig. 3. Bare and screened potentials for hexatriene; (a) bare potential, (b) $\hat{\Gamma}^1$ screened potential, (c) $\hat{\Gamma}^3$ screened potential

Table 5. The lowest excitation energies for hexatriene (in eV)

	Bare	$\hat{\Gamma}^3$ Screened	$\hat{\Gamma}^1$ Screened	Exp.[23]
1_{B_u}	5.42	4.43	4.53	5.09
	8.93	6.80	7.42	
1_{A_g}	7.58	5.83	6.29	
	7.90	9.27	8.78	
3_{B_u}	—	3.32	2.51	2.6
	—	5.11	4.57	
3_{A_g}	—	4.35	3.69	
	7.58	9.27	8.78	

Table 6. Screened potential values for phenol (in eV)

The values in the upper triangle are $\hat{\Gamma}^1$ screened potentials, while the values in the lower triangle are $\hat{\Gamma}^3$ screened potentials. Bare potentials are as follows; $\gamma_{11}=17.31$, $\gamma_{12}=9.09$, $\gamma_{13}=5.69$, $\gamma_{14}=4.99$, $\gamma_{17}=9.53$, $\gamma_{27}=5.82$, $\gamma_{37}=3.88$, $\gamma_{47}=3.43$, $\gamma_{77}=26.09$. $\beta_{CO}=-2.50$, $I_p(O)=33.90$, C–C 1.39 Å, C–O 1.36 Å.



	1	2	3	4	5	6	7	
	12.77	8.76	7.00	7.08	7.00	8.76	7.86	1
		12.34	8.75	6.87	6.99	6.91	6.82	2
1	11.47		12.49	8.69	6.91	6.99	5.63	3
2	8.57	10.96		12.34	8.69	6.87	5.91	4
3	7.49	8.54	11.10		12.49	8.75	5.63	5
4	7.69	7.34	8.46	10.95		12.34	6.82	6
5	7.49	7.56	7.37	8.46	11.10		18.75	7
6	8.57	7.39	7.56	7.34	8.54	10.96		
7	7.34	6.97	6.20	6.54	6.20	6.97	16.87	

Table 7. The lowest excitation energies for phenol (in eV)

	Bare	$\hat{\Gamma}^3$ Screened	$\hat{\Gamma}^1$ Screened	Exp.
1_{A_1}	5.72	4.56	4.62	5.82[24]
	7.35	5.69	6.19	6.93
1_{B_2}	4.59	4.60	4.69	4.59
	7.54	5.81	6.29	6.70
3_{A_1}	—	3.50	2.71	3.54[25]
	3.48	4.37	4.23	
3_{B_2}	3.16	4.07	3.98	
	4.18	5.04	5.05	

3.3. Phenol

Table 6 contains the bare and screened potentials of phenol, and Table 7 contains the corresponding excitation energies. As shown in the other molecules presented in this study, the $\hat{\Gamma}^3$ screened potential gave more adequate values than the $\hat{\Gamma}^1$ ones for the triplet excitation energies.

4. Conclusion

The effective interaction was expanded by the polarization propagators whose vertex parts correspond to either the singlet or the triplet excitation, and the excitation energies of the π-electron systems were calculated. The one-center screened potential, $\tilde{\gamma}_{11}$, was calculated to be much smaller than the bare potential, γ_{11}. The two-center screened potential, $\tilde{\gamma}_{rs}$, decreased with the distance between r and s more slowly than the bare potential, γ_{rs}. These results show that π-electrons move nonlocally in a molecule.

The Coulson–Rushbrooke theorem in alternant hydrocarbons broke down [7, 22] in Little's method, because of insufficient consideration of the correlation effects. There was, however, no such case in the present screened potential calculation. Excitation energies calculated by the present screened potential method were in good agreement with the observed values, and the triplet instability which appeared in the RPA calculation was removed. The $\hat{\Gamma}^3$ screened potential was more effective for the triplet excitations than $\hat{\Gamma}^1$. However, the large difference between the two potentials was not found in the case of singlet excitations.

Acknowledgments. The author would like to acknowledge Professor K. Suzuki and Professor Y. J. I'Haya for their continuing interest and encouragement. Thanks are also due to Dr. O. Kikuchi and Dr. T. Morikawa for reading the manuscript, and to Dr. S. Narita for useful comments.

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Received October 26, 1977/February 13, 1978