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Self-Consistent Renormalized RPA: The Electronic Excited States of Benzene in the INDO/S Method

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Synopsis. A self-consistent renormalized RPA and its approximated analogues are compared in the calculation of the electronic excited states of benzene by using the INDO/S method.

In previous papers,[1,2] we have presented an approximate self-consistent renormalized random-phase approximation (SCrRPA) with the CNDO/S method and shown that making use of a well-correlated ground state charge density the rRPA equation can be self-consistently solved though approximately. In this note, we like to present the result of the complete SCrRPA calculation for benzene and compare it with those of the approximate SCrRPA ones. We use the INDO/S basis, since the CNDO method has a deficiency that energy separations between the singlet and triplet levels of both $\sigma\pi^*$ and $\pi\sigma^*$ states are calculated to be zero in high-symmetry molecules like benzene.

For the real basis, the rRPA equation is given by[3,4]

$$\begin{pmatrix} \tilde{\boldsymbol{A}}(S) & -\tilde{\boldsymbol{B}}(S) \\ -\tilde{\boldsymbol{B}}^*(S) & -\tilde{\boldsymbol{A}}^*(S) \end{pmatrix} \begin{pmatrix} \tilde{\boldsymbol{Y}}(\lambda S) \\ \tilde{\boldsymbol{Z}}(\lambda S) \end{pmatrix} = \omega_\lambda \begin{pmatrix} (\tilde{\boldsymbol{Y}}\lambda S) \\ \tilde{\boldsymbol{Z}}(\lambda S) \end{pmatrix}, \tag{1}$$

where

$$\tilde{A}_{\mathrm{ph,vf}}(S) = \delta_{\mathrm{pv}}\delta_{\mathrm{hf}}(E_{\mathrm{p}}-E_{\mathrm{h}}) + (1/2)(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}(\rho_{\mathrm{f}}-\rho_{\mathrm{v}})^{1/2} \times (A^0_{\mathrm{ph.vf}}(S)-\delta_{\mathrm{pv}}\delta_{\mathrm{hf}}(E_{\mathrm{h}}-E_{\mathrm{p}})),$$

$$\tilde{B}_{\mathrm{ph,vf}}(S) = (1/2)(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}(\rho_{\mathrm{f}}-\rho_{\mathrm{v}})^{1/2}B^0_{\mathrm{ph.vf}}(S).$$

A^0 and B^0 are the well-known normal RPA(nRPA) matrices for the HF ground state, E_i the ith HF orbital energy, ρ_i the charge density (non-integral occupation number) of the ith MO in the correlated RPA ground state. Subscripts *ph* and *vf* are used for the particle-hole and vacant-filled MO pair states, respectively. We are interested in the cases except $\rho_{\mathrm{h}}=\rho_{\mathrm{f}}=2$ and $\rho_{\mathrm{p}}=\rho_{\mathrm{v}}=0$ (nRPA), which correspond to a higher RPA and are referred to merely as RPA in the following. The renormalized transition amplitudes matrices $\tilde{\boldsymbol{Y}}$ and $\tilde{\boldsymbol{Z}}$ are given by the unrenormalized ones $\boldsymbol{Y}$ and $\boldsymbol{Z}$.[5] The λth excited state creation operator $\mathrm{O}^+_{\lambda SM}$ which satisfies $\mathrm{O}^+_{\lambda SM}|0\rangle=|\lambda SM\rangle$ is expanded in terms of the singly excited unrenormalized amplitudes $Y_{\mathrm{ph}}(\lambda S)$ and $Z_{\mathrm{ph}}(\lambda S)$ and the particle-hole pair creation and annihilation operators $C^+_{\mathrm{ph}}(SM)$ and $C_{\mathrm{ph}}(\overline{SM})$. The correlated RPA ground state is unknown before solving Eq. 1 and is assumed to take the form

$$|0\rangle = N_0 \mathrm{e}^U|\mathrm{HF}\rangle \tag{2}$$

with

$$U = (1/2)\sum_{S=0.1}\sum_{i}\sum_{\mathrm{ph}\in\Gamma_i}\sum_{\mathrm{vf}\in\Gamma_i} C_{\mathrm{ph,vf}}(S)\,C^+_{\mathrm{ph}}(S0)\,C^+_{\mathrm{vf}}(\overline{S0}), \tag{3}$$

$$\Gamma_i \times \Gamma_i \in \Gamma_{\mathrm{HF}},$$

Γ being denote the irreducible representation of a certain set of the excited states under consideration, and N_0 the normalization constant. $C_{\mathrm{ph,vf}}(S)$ in Eq. 3 is then given by a solution of the equation

$$\mathrm{O}_{\lambda SM}|0\rangle = 0 \qquad (\text{all } \lambda SM), \tag{4}$$

leading to the equation $\boldsymbol{Z}=\boldsymbol{CY}$ and/or $\tilde{\boldsymbol{Z}}=\boldsymbol{C}\tilde{\boldsymbol{Y}}$. Assuming the starting value of $C_{\mathrm{ph,vf}}(S)$ under this constraint, we can determine by an iterative prodecure the occupation number of the ith MO averaged with respect to a trial ground state. Invoking the identity, operator $\times\,\mathrm{e}^U$, we can derive the correlated charge densities of the uth particle and oth hole states averaged according to the correlated RPA ground state as follows;

$$\rho_{\mathrm{u}} = 2^{1/2}\langle 0|C^+_{\mathrm{uu}}(00)|0\rangle = (1/2)\sum_{s}\sum_{\mathrm{h}}\sum_{\mathrm{vf}}|C_{\mathrm{uh,vf}}(S)|^2, \qquad (\text{for all } \Gamma_i) \tag{5}$$

and

$$\rho_0 = 2^{1/2}\langle 0|C^+_{\mathrm{oo}}(00)|0\rangle = 2-(1/2)\sum_{s}\sum_{\mathrm{p}}\sum_{\mathrm{vf}}|C_{\mathrm{po,vf}}(S)|^2. \qquad (\text{for all } \Gamma_i) \tag{6}$$

In order to circumbent the triplet instability at an initial stage, we start a computation by making use of the following trial correlated coefficients of a ground state wavefunction,[6] so as to satisfy the equation $\tilde{\boldsymbol{Z}}=\boldsymbol{C}\tilde{\boldsymbol{Y}}$;

$$C^{\mathrm{trial}}_{\mathrm{ph.vf}}(S) = (E_{\mathrm{p}}+E_{\mathrm{v}}-E_{\mathrm{h}}-E_{\mathrm{f}})^{-1}B^0_{\mathrm{ph.vf}}(S). \tag{7}$$

We can then iteratively determine new renormalized coefficients as[7,8]

$$\boldsymbol{C}^{\mathrm{new}}(S) \approx (\tilde{\boldsymbol{Y}}^{-1}(S)\tilde{\boldsymbol{Z}}(S))^{\mathrm{trial}}. \tag{8}$$

The convergence criterion used is $|\rho_i(\mathrm{new})-\rho_i(\mathrm{old})| \leqq 10^{-5}$ (i for all the MO's).

The summation over i of Γ_i indicates that the excited states of different symmetry groups affect the correlated ground state. Therefore, if possible, it is better to solve such an rRPA equation that all the possible particle-hole pair configurations are involved in a one matrix, without paying attention to a special symmetry representation. At least for the RPA equation of limited particle-hole pairs this may play a considerable role in the computation of ρ's.

In our previous SCF calculation of benzene by the INDO/S method,[9] the ground-state electronic configuration was given by

$$(1a_{1g})^2(2,3e_{1u})^4(4,5e_{2g})^4(6a_{1g})^2(7b_{1u})^2(8b_{2u})^2(9,10e_{1u})^4$$
$$(11\pi a_{2u})^2(12,13e_{2g})^4(14\pi,15\pi e_{1g})^4(16\pi,17\pi e_{2u})^0$$
$$(18b_{2u})^0(19\pi b_{2g})^0(20,21e_{2g})^0(22a_{1g})^0(23,24e_{1u})^0$$
$$(25b_{1u})^0(26,27e_{1u})^0(28,29e_{2g})^0(30a_{1g})^0.$$

From this, we take *thirty* particle-hole pair configuration, in which we promote an electron from *five* MO's below the highest occupied orbital to *six* MO's above the lowest unoccupied orbital. Then, we solve a 60×60 matrix of the rRPA equation involving $\sigma\pi^*$, $\pi\sigma^*$, $\sigma\sigma^*$, and $\pi\pi^*$ particle-hole pairs, iteratively. For comparison,

TABLE 1. EXCITATION ENERGIES (eV) OF BENZENE COMPUTED BY THE RPA EQUATIONS CONSTRUCTED FROM THIRTY SIGMA-PI PARTICLE HOLE PAIRS[a]

State	SCrRPA	rRPA/CI	rRPA/RS	TDA	nRPA	Obsd[c]
$^1B_{2u}(\pi\pi^*)$[b]	5.07	4.97	4.86	4.90	4.76	4.93
$^1B_{1u}(\pi\pi^*)$	5.46	5.36	5.27	5.21	5.18	6.21
$^1E_{1u}(\pi\pi^*)$	6.92 (1.324)[d]	6.84 (1.321)	6.76 (1.316)	7.23 (2.070)	6.68 (1.310)	6.96 (0.690)
$^1A_{2u}(\sigma\pi^*)$	7.97 (0.003)	7.92 (0.003)	7.86 (0.003)	7.82 (0.003)	7.82 (0.003)	
$^1E_{2u}(\pi\sigma^*)$	8.00	7.95	7.89	7.88	7.84	
$^1E_{2u}(\pi\sigma^*)$	8.10	8.05	7.99	7.95	7.95	
$^1A_{1u}(\sigma\pi^*)$	8.17	8.12	8.07	8.02	8.02	
$^1E_{2g}(\pi\pi^*)$	8.20	8.13	8.07	8.15	8.03	
$^3B_{1u}(\pi\pi^*)$	2.90	2.72	2.55	3.04	2.39	3.95
$^3E_{1u}(\pi\pi^*)$	4.58	4.46	4.35	4.26	4.25	4.75
$^3B_{2u}(\pi\pi^*)$	5.07	4.97	4.86	4.90	4.76	5.60
$^3E_{2g}(\pi\pi^*)$	6.33	6.22	6.15	6.11	6.08	6.75
$^3E_{2u}(\pi\sigma^*)$	7.30	7.24	7.18	7.16	7.13	

a) Geometry: C–C 1.40 Å; C–H 1.10 Å. b) Symbols in braces show the main contribution. c) J. Karwowski, *Acta Phys. Pol. A*, **37**, 417 (1970). d) Figures in braces are the values of oscillator strength.

TABLE 2. PURE $\pi\pi^*$ EXCITATION ENERGIES (eV) OF BENZENE, FOR WHICH NINE $\pi\pi^*$ PARTICLE-HOLE PAIR CONFIGURATIONS ARE TAKEN FROM THE INDO/S BASIS MO'S[a]

State	SCrRPA	rRPA/CI	rRPA/RS	TDA	nRPA
$^1B_{2u}$	5.06	4.98	4.85	4.90	4.76
$^1B_{1u}$	5.45	5.37	5.26	5.21	5.18
$^1E_{1u}$	7.07 (1.572)	7.00 (1.565)	6.91 (1.554)	7.44 (2.553)	6.84 (1.545)
$^1E_{2g}$	8.25	8.21	8.13	8.22	8.08
$^1E_{2g}$	10.48	10.44	10.37	10.39	10.33
$^1B_{1u}$	12.82	12.81	12.77	12.79	12.76
$^3B_{1u}$	2.88	2.74	2.53	3.04	2.39
$^3E_{1u}$	4.56	4.47	4.34	4.26	4.25
$^3B_{2u}$	5.06	4.98	4.85	4.90	4.76
$^3E_{2g}$	6.32	6.26	6.15	6.12	6.08
$^3E_{2g}$	10.07	10.03	9.96	9.92	9.92
$^3B_{1u}$	12.42	12.41	12.37	12.36	12.36

a) See the footnotes of Table 1.

we calculate pure $\pi\pi^*$ excitations taking nine $\pi\pi^*$ particle-hole pair configurations.

Without solving Eq. 1 iteratively, the coefficients $C_{\mathrm{ph,vf}}(S)$ can be approximately determined either (i) by using the perturbation theory in the CI language to include doubly excited configurations which mix with the HF ground state (referred to as rRPA/CI), or (ii) by relating $C_{\mathrm{ph,vf}}(S)$ with $B^0_{\mathrm{ph,vf}}(S)$ matrix in the basis of Rayleigh-Schrödinger perturbation theory (Eq. 7) (as rRPA/RS). With the trial RPA ground state to be obtained in such ways, we can bypass the problem of solving Eq. 4, in case when the trial coefficients satisfy Eq. 4 approximately. These methods have been called an approximate SCrRPA in our previous paper.[5]

The numerical results are summarized in Tables 1 and 2. The SCrRPA results satisfactorily agree with the experimental values except for the lowest $^3B_{1u}$ state. The self-consistency has been attained after nine iterations. It should be mentioned that we have fixed the correlated charge densities as $\rho(\mathrm{new'})=(1/2)\times\{\rho(\mathrm{new})+\rho(\mathrm{old})\}$ at every iterative step in order to get a quick convergence. It is observed that the following relationship holds for most cases:

$$\omega(\mathrm{rRPA}) > \omega(\mathrm{TDA}) > \omega(\mathrm{nRPA}) \tag{9}$$

or in more detail

$$\omega(\mathrm{SCrRPA}) > \omega(\mathrm{rRPA/CI}) > \omega(\mathrm{rRPA/RS}) > \omega(\mathrm{TDA}) > \omega(\mathrm{nRPA}). \tag{10}$$

The $^1E_{1u}$ and $^3B_{1u}$ transition energies fall out of this sequence, for which $\omega(\mathrm{TDA})>\omega(\mathrm{SCrRPA})$. It has been numerically ascertained that this sequence also holds for the electronic excited states of DNA bases in the CNDO/S method.[5] The treatment including σ electrons (Table 1) gives rise to the considerable lowering of the transition energy and oscillator strength of the dipole-allowed $^1E_{1u}$ transition, compared with that of the π electrons only (Table 2). This can be ascribed to the sigma-pi coupling; *i.e.*, the so-called dynamical screening effect of the $\pi\pi^*$ transition by σ electrons which has been pointed out previously by several authors.[10,11]

The sequence of Eq. 10 and Table 1 indicates that rRPA/CI promises to give a good approximation to SCrRPA, and that the correlated ground-state wavefunction (HF+doubly excited CI's) takes in the triplet correlation effect through $B^0_{\mathrm{ph,vf}}(S)$ matrix elements in a somewhat skillful way. It might also be concluded that to solve the nRPA equation with a partinent choice of parameters in the semiempirical MO methods rivals a higher RPA, fully accounting the correlation effect in large conjugated systems. This can also be visualized in a Green's function language; *i.e.*, the use of the CNDO/S and/or INDO/S parametrization together with nRPA has a drastic effect upon the self-energy part, leaving the zero-order polarization propagator unaffected.[12]

Comparison of the present semiempirical results with the *ab initio* ones computed by Rose *et al.*[10] suggests that if the present restricted configurational space is extended the lowest $^3B_{1u}$ state will be refined. This possibility can be observed from the inspection of Tables 1 and 2, where the sigma-pi coupling effect puts the lowest $^3B_{1u}$ state a little bit up. Extensive calculation including a larger particle-hole pair space is now in progress.

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