Absorption Spectra from Bethe Salpeter Equation

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I. EXCITON AFFAIRS IN CRYSTAL: BETHE SALPETER EQUATION OF MOTION

Excitonic affairs are governed by a two-particle (electron and hole) Dyson-like equation of motion. In a ladder-approximation representation [1],

$$\mathcal{L}\left(12;1^{'}2^{'}\right)=\mathcal{L}_0\left(12;1^{'}2^{'}\right)+\int d\left(3456\right)\mathcal{L}_0\left(14;1^{'}3\right)K\left(35;46\right)\mathcal{L}\left(62;52'\right) \tag{1}$$

in which $\mathcal{L}\left(12;1^{'}2^{'}\right)$ and $\mathcal{L}_0\left(12;1^{'}2^{'}\right)$ are the interacting and non-interacting two-particle Green's propagator respectively. The variable "(1)" (and similar others) is a short hand notation for the spatial, spin and four time (two creation and two annihilation) coordinates: $(1)\equiv(r_1,\sigma_1,t_1)$ respectively. In case of occupied (v) and unoccupied (c) states, $\mathcal{L}_0$ in Fourier transform plane has the form

$$\mathcal{L}_0^{vcv'c'}\left(\omega\right)=\frac{1}{\omega-\left(E_c^{DFT}-E_v^{DFT}\right)+i\eta}\delta_{cc'}\delta_{vv'} \tag{2}$$

Note here that the four time variables are now decomposed in a single frequency in the ω plane.
The kernel $K_{vc\mathbf{k}v'c'\mathbf{k}'}$ is a functional static quantity and is the sum of a bare exchange Coulomb repulsion and statically screened Coulomb attraction between the electron and hole. The latter is represented as

$$\mathrm{W}\left(vc\mathbf{k};v'c'\mathbf{k}'\right)=\frac{1}{\Omega}\sum_{\mathbf{GG'}}v\left(\mathbf{q}+\mathbf{G}'\right)\epsilon^{-1}_{\mathbf{GG'}}\left(\mathbf{q}\right)\times\left\langle v'\mathbf{k}'\left|e^{-i\left(\mathbf{q}+\mathbf{G}'\right).\mathbf{r}}\right|v\mathbf{k}\right\rangle\left\langle c\mathbf{k}\left|e^{i\left(\mathbf{q}+\mathbf{G}'\right).\mathbf{r}}\right|c'\mathbf{k}'\right\rangle\delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'} \tag{3}$$

while the former is

$$V\left(vc\mathbf{k};v'c'\mathbf{k}'\right)=\frac{1}{\Omega}\sum_{\mathbf{G}\neq0}v\left(\mathbf{G}\right)\left\langle v'\mathbf{k}'\left|e^{-i\mathbf{G}.\mathbf{r}}\right|c'\mathbf{k}'\right\rangle\times\left\langle c\mathbf{k}\left|e^{i\mathbf{G}.\mathbf{r}}\right|v\mathbf{k}\right\rangle \tag{4}$$

where Ω in this case is the cell volume. K is thus defined as $K_{vc\mathbf{k};v'c'\mathbf{k}'}=\left\langle vc\mathbf{k}\left|\mathrm{W}-2V\right|v'c'\mathbf{k}'\right\rangle$. It is in this statically screened kernel W in which the $\mathrm{G_0W_0}$ QP energies are included to get the correct transition energies. Note that in order to obtain a solvable BSE [2], W is approximated to be a static, which can be borrowed from the preceding dynamic screening calculations in $\mathrm{G_0W_0}$ simply by putting ω=0.
Assuming that the off-diagonal elements in the self-energies are small which consequently makes the total Hamiltonian to be a Hermitian and the QP states orthogonal, the exciton EOM (i.e., the BSE) becomes [1]

$$\left(E^{QP}_{c\mathbf{k}}-E^{QP}_{v\mathbf{k}}\right)A^s_{vc\mathbf{k}}+\sum_{v'c'\mathbf{k}'}\left\langle vc\mathbf{k}\left|K_{vcv',v'c'\mathbf{k}'}\right|v'c'\mathbf{k}'\right\rangle A^s_{vc\mathbf{k}}=E^S_X A^s_{vc\mathbf{k}} \tag{5}$$

in which S is each exciton (i.e., a pair state with a distinct principal quantum number and momentum wave-vector difference between v and c), E_X is the excitonic energy that is obtained by diagonalizing this Hamiltonian and $A^s_{vc\mathbf{k}}$ is the excitonic amplitude in the electron-hole basis and contains the light polarization direction. As the momentum wave-vector difference is zero for vertical transitions, therefore excitons with such transitions (bright excitons) are only detectable. The resonant Green's propagator is then

$$\mathcal{L}_{vc,v'c'}\left(\omega\right)=\sum_S\frac{A_{vc\mathbf{k}^S}A^{S*}_{v'c'\mathbf{k}'}}{\omega-E_X+i\eta} \tag{6}$$

The numerator can be obtained via residue theorem and signifies the exciton oscillator strength. The macroscopic dielectric function (i.e., the absorption spectra) is thus evaluated in limit of long wavelength $\mathbf{q}\rightarrow0$ [1]

$$\varepsilon_M\left(\omega\right)=1-\lim_{\mathbf{q}\rightarrow0}\left(\frac{8\pi}{|q|^2\Omega}\right)\sum_{vck}\sum_{v'c'k'}\langle v\mathbf{k}-\mathbf{q}|e^{-i\mathbf{qr}}|c\mathbf{k}\rangle\times\langle c'\mathbf{k}'|e^{i\mathbf{qr}}|v'\mathbf{k}'-\mathbf{q}\rangle\sum_S\left(\frac{A^S_{vc\mathbf{k}}A^{S*}_{v'c'\mathbf{k}'}}{\omega-E_X+i\eta}\right) \tag{7}$$

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This is also the linear response function $\chi_{ij}^{(1)}(\omega)$.
In order to analyse if the exciton is "Frenkel" or "Wannier"-type, the exciton wave-function is needed. This can be written as

$$\left|\Phi^{S}\left(\mathbf{r}_{e},\mathbf{r}_{h}\right)\right\rangle=\sum_{vc\mathbf{k}}A_{vc\mathbf{k}}^{S}\phi_{v\mathbf{k}}\left(\mathbf{r}_{e}\right)\phi_{c\mathbf{k}}\left(\mathbf{r}_{h}\right)\tag{8}$$

in which $\mathbf{r}_e$ and $\mathbf{r}_h$ are the electron and hole coordinates in real-space. We note that the evaluation of this wave-function would require six-coordinates.

[1] M. Rohlfing and S. G. Louie, Phys. Rev. B **62**, 4927 (2000).
[2] A. Marini and R. DelSole, Phys. Rev. Lett. **91**, 176402 (2003).