Effects of the Electron–Hole Interaction on the Optical Properties of Materials: the Bethe–Salpeter Equation

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Abstract

In these notes, the two-particle Hamiltonian for electron–hole interaction is derived. First, a simple Hartree–Fock based approach is used and an effective two-particle Schrödinger equation is obtained. Then, using Green's function techniques of many-body perturbation theory, correlation effects are introduced and the Bethe–Salpeter equation is deduced, where the electron–hole interaction is partially screened. Finally, some significant results in the literature are discussed.

1. Introduction

An ensemble of N interacting electrons can in principle be described in terms of a wavefunction which depends on N coordinates. The solution of the time-independent Schrödinger equation gives details about the ground state and the excited states of the system, while the time-dependent equation describes the evolution of the system in the presence of an external perturbation. However, when N is larger than five, the solution is already a formidable task, which quickly becomes impossible as the number of electrons increases. In the last decades, the development of density functional theory [1,2] (DFT) in the Kohn–Sham formulation [3] has shown that a theoretically sound description of the many-electron ground state is possible through the solution of an effective single-particle Schrödinger equation; the only similarity between the true many-body Hamiltonian and the effective one is that they give the same charge density. The DFT has been recently extended to the time-dependent DFT formalism [4] allowing the inclusion of a time-dependent external potential and the study of the excited states, which are indeed the key quantities for the description of spectroscopic measurements like electron-energy loss and optical absorption. The main difficulty in the DFT is that the exact effective exchange-correlation potential, which includes correlation effects, is unknown. In particular, while very simple forms for this potential [such as the local density approximation (LDA)] yield very good results for the ground state properties, the excited-state and time-dependent properties are usually much more difficult to obtain.

An alternative approach to the calculation of excited-states properties is based on many-body perturbation theory [5,6], where relatively simple quantities like one-particle or two-particle Green's functions are used to decribe only the interesting properties of the true many-particle wavefunction. In particular, the one-particle Green's functions is defined in such a way that the propagation of a single electron added to the N electron ground state is described exactly. The excited states of the $(N + 1)$ [or $(N − 1)$]-particle systems are interpreted as propagating single-electron (or single-hole) excitations, and are treated as if they were a collection of nearly non-interacting quasiparticles [7,8]. An effective one-particle Hamiltonian can be found that describes these quasi-particles, and a systematic way of predicting experiments involving $N − 1$ or $N + 1$ electrons, like photoemission or inverse photoemission, is obtained, together with a consistent theoretical justification for the single-electron model. Moreover, the study of the excited states of the N electron system can be carried out in the useful scheme of interacting quasielectron–quasihole pairs, usually referred to as excitons; the description of the quasielectron–quasihole interaction, and how this interaction is affected by the presence of other electrons, can be achieved with very controlled approximations. This formalism leads to an effective two-particle Schrödinger equation known as the Bethe–Salpeter equation. The recent success of this method is impressive: absorption experiments can be simulated with a precision of 10% for the peak positions and 20% for the peak strengths [9].

These lecture notes are largely based on published reviews [8,9], which are suggested for further reading. In particular, Ref. [8] contains a concise but significant overview of Green's function techniques, while in Ref. [9] a very in-depth comparison between the Bethe–Salpeter equation and the time-dependent DFT can be found. For a more in-depth study of the formalism of Green's function theory the reader is invited to refer to standard textbooks [5,6], while a more basic treatment of the optical properties of solids, together with simpler models for the electron–hole interaction, can be found in Ref. [10].

2. The two-particle Hamiltonian

In this section, a simplified approach for the inclusion of correlation effects in a many-electron system will be used to find an effective Hamiltonian for the interacting electron–hole pair. In particular, the evolution of a system in the presence of an external perturbation will be described in the Hartree–Fock approximation, leading to the effective two-particle Hamiltonian. This approach can be used without reference to the somewhat complex Green's

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function formalism, which will be introduced in the next section.

2.1. *Hartree–Fock approximation*

One of the simplest approaches to the many body problem is the Hartree–Fock approximation (HFA) [11]. In the HFA, the many body wavefunction of the ground state is approximated as a single Slater determinant

$$|N^{\text{HFA}}\rangle = \frac{\det_{kl}\{u_k(x_l)\}}{\sqrt{N!}}. \tag{1}$$

The total energy of the system is then found by taking the expectation value of the real many-body Hamiltonian in this approximate, trial state. The set $\{u_k(x)\}$ of single-particle states which form the HFA ground state is obtained by minimizing the energy with respect to the wavefunction, subject to the constraint that the wavefunctions are normalized. We have

$$\frac{\delta}{\delta u_i(x)}\left[\langle N^{\text{HFA}}|\hat{H}|N^{\text{HFA}}\rangle - \omega_i \int dx |u_i(x)|^2\right] = 0, \tag{2}$$

for each value of *i*. In this way, the Slater determinants which are lower in energy, and thus closest to the correct many-body wavefunction, are found. This constrained minimization problem with Lagrangian multipliers $\{\omega_i\}$ reduces to a single-particle, eigenvalue problem

$$[\omega_i - h(x) - V_{\text{H}}(x)]u_i(x) - \int V_{\text{ex}}(xx')u_i(x')\,dx' = 0, \tag{3}$$

with the definitions:

$$V_{\text{H}}(x) = \int v(xx')\rho(x')\,dx', \tag{4a}$$

$$V_{\text{ex}}(x_1 x_2) = -v(x_1 x_2)\rho(x_1 x_2). \tag{4b}$$

The term $h(x)$ represents the single-particle part of the true Hamiltonian (kinetic plus external potential). V_{H} is the local Hartree potential due to the average electronic density, while V_{ex} is the non-local exchange operator, which is proportional to the density matrix. $v(xx')$ is the bare Coulomb interaction. It is equal to $e^2/|x - x'|$. The many-electron problem is transformed into a single-electron problem, and the effect of the other electrons is reduced to an effective single-particle Hamiltonian, which self-consistently depends on the total density of the system. The part of the single-particle Hamiltonian due to the interaction with the other electrons is referred to as the internal potential, as opposed to the external potential contained in $h(x)$: in the HFA the internal potential is $V_{\text{int}} = V_{\text{H}} + V_{\text{ex}}$.

2.2. *Introduction of a perturbation*

Now we can ask ourselves what happens if an external and possibly non-local potential is added as a perturbation, that is $h \to h + \delta V_{\text{ext}}$. This is a subtle problem, because a change in the external potential modifies the Hartree–Fock orbitals which in turn change the self-consistent internal potential in the Hartree–Fock Hamiltonian. We also assume that the time dependence of the external potential

is $e^{i\omega t}$ with a given frequency ω. Since the Hartree–Fock Hamiltonian is a function of the non-local density matrix, we define a four-point total response function $^4\chi$ as the functional derivative of the density matrix with respect to the external perturbation

$$^4\chi(x_1 x_2 x_3 x_4) = \frac{\delta\rho(x_1 x_2)}{\delta V_{\text{ext}}(x_3 x_4)}. \tag{5}$$

To first order in the perturbation, we have

$$\delta\rho(x_1 x_2) = \int {}^4\chi(x_1 x_2 x_3 x_4)\delta V_{\text{ext}}(x_3 x_4)\,dx_3\,dx_4. \tag{6}$$

The response function depends implicitly on the frequency of the perturbation. We also introduce an independent-particle four-point response, $^4\chi_0$, which also depends on the frequency ω, defined as

$$^4\chi_0(x_1 x_2 x_3 x_4) = \frac{\delta\rho(x_1 x_2)}{\delta V_{\text{tot}}(x_3 x_4)}, \tag{7}$$

where δV_{tot} is the variation of the total (i.e., external plus internal) potential. We now assume that the independent-particle response is known (it can be easily obtained through first order perturbation theory as shown in appendix I) and we seek the relationship between $^4\chi$ and $^4\chi_0$. We first write the response as

$$^4\chi(x_1 x_2 x_3 x_4) = \int \frac{\delta\rho(x_1 x_2)}{\delta V_{\text{tot}}(x_5 x_6)}\frac{\delta V_{\text{tot}}(x_5 x_6)}{\delta V_{\text{ext}}(x_3 x_4)}\,dx_5\,dx_6. \tag{8}$$

Recalling that $\delta V_{\text{tot}} = \delta V_{\text{ext}} + \delta V_{\text{int}}$ and omitting the explicit spatial coordinates, we write $^4\chi$ as a matrix product

$$^4\chi = \frac{\delta\rho}{\delta V_{\text{tot}}}\left(\frac{\delta V_{\text{ext}}}{\delta V_{\text{ext}}} + \frac{\delta V_{\text{int}}}{\delta V_{\text{ext}}}\right) = {}^4\chi_0\left(1 + \frac{\delta V_{\text{int}}}{\delta\rho}{}^4\chi\right). \tag{9}$$

Defining the four-point kernel $K = \delta V_{\text{int}}/\delta\rho$, we obtain the Dyson's equation

$$^4\chi = {}^4\chi_0 + {}^4\chi_0 K {}^4\chi. \tag{10}$$

In the HFA, the explicit form of the internal potential is

$$V_{\text{int}}(x_1 x_2) = \delta(x_1 x_2)\int v(x_1 x)\rho(xx)\,dx - v(x_1 x_2)\rho(x_1 x_2), \tag{11}$$

and the kernel K is

$$K(x_1 x_2 x_3 x_4) = v(x_1 x_3)\delta(x_1 x_2)\delta(x_3 x_4) +$$
$$- v(x_1 x_2)\delta(x_1 x_3)\delta(x_2 x_4). \tag{12}$$

The first term comes from the Hartree potential, and the second from the exchange potential.

2.3. *Two particle effective equation*

Equation (10) can in principle be solved by inverting a four-point matrix for each possible frequency ω

$$^4\chi = (1 - {}^4\chi_0 K)^{-1}\,{}^4\chi_0. \tag{13}$$

However, the physical picture of interacting electron–hole pairs suggest reformulating the problem as an effective eigenvalue problem. This derivation of the two-particle

Hamiltonian is taken essentially from Ref. [9]. If a basis of eigen-functions $u_k(x)$ of the effective single-particle Hamiltonian are used, one can assume that only a limited number of electron–hole pairs contribute to each excitation. Any four-point quantity $S(x_1x_2x_3x_4)$ can be written as

$$S(x_1x_2x_3x_4) = \sum_{n_1n_2n_3n_4} u_{n_1}^*(x_1)u_{n_2}(x_2)\times$$

$$\times u_{n_3}(x_3)u_{n_4}^*(x_4)S_{(n_1n_2)(n_3n_4)}. \quad (14)$$

The independent-particle response derived in appendix I is diagonal in this basis and reads ${}^4\chi_{0(n_1n_3)(n_2n_4)} = (f_{n_2} - f_{n_1})\delta_{n_1n_3}\delta_{n_2n_4}(\omega_{n_2} - \omega_{n_1} - \omega)^{-1}$. Note that the response is a singular matrix for every value of ω: zeros on the diagonal appear when the occupation factors f_{n_1} and f_{n_2} are equal. In this matrix notation, we introduce an occupation matrix $F_{(n_1n_2)(n_3n_4)} = (f_{n_2} - f_{n_1})\delta_{n_1n_3}\delta_{n_2n_4}$. We also define an invertible response ${}^4\breve{\chi}_0$ which is diagonal and (i) equal to the singular response ${}^4\chi_0$ for those elements satisfying $f_{n_2} \neq f_{n_1}$, while it is set to (ii) a finite arbitrary value otherwise. Omitting the state indices, we write ${}^4\chi_0 = {}^4\breve{\chi}_0 F$ as a matrix product. We therefore have

$${}^4\chi = (1 - {}^4\breve{\chi}_0 FK)^{-1}\,{}^4\breve{\chi}_0 F = ({}^4\breve{\chi}_0^{-1} - FK)^{-1}F. \quad (15)$$

Due to the fact that the ${}^4\breve{\chi}_0$ is diagonal and to the presence of the F factors, the elements with both indices (n_1n_2) occupied or both unoccupied are irrelevant for the calculation of the ${}^4\chi$. The same holds for (n_3n_4). This is meaningful, because only transitions between occupied and empty states are involved in the electronic polarization. From this point on, only the block which satisfies this condition will be considered. We can now show explicitly the frequency dependence of the independent-particle response writing

$${}^4\chi = ({}^4\breve{\chi}_0^{-1}(\omega = 0) - FK - \omega)^{-1} = (H^{2p} - \omega)^{-1}$$

for $(f_{n_2} - f_{n_1}) \neq 0$ and $(f_{n_4} - f_{n_3}) \neq 0$, $\quad (16)$

where we have defined the two particle effective Hamiltonian as $H^{2p} = {}^4\breve{\chi}_0^{-1}(\omega = 0) - FK$.
     The explicit form of the matrix H^{2p} is now

$$H^{2p}_{(n_1n_2)(n_3n_4)} = (\omega_{n_2} - \omega_{n_1})\delta_{n_1n_3}\delta_{n_2n_4} + (f_{n_2} - f_{n_1})K_{(n_1n_2)(n_3n_4)}, \quad (17)$$

which is not generally Hermitian. In block form, it is

$$H^{2p} = \begin{pmatrix} H^{2p,res} & H^{coupling} \\ -[H^{coupling}]^* & -[H^{2p,res}]^* \end{pmatrix}. \quad (18)$$

Here $H^{2p,res}$ is the resonant part which corresponds to interaction between occupied→empty transitions $[(f_{n_2} - f_{n_1}) = (f_{n_4} - f_{n_3}) = 1]$, the antiresonant part $-[H^{2p,res}]^*$ contains interaction between empty→occupied transitions $[(f_{n_2} - f_{n_1}) = (f_{n_4} - f_{n_3}) = -1]$. The $H^{coupling}$ and $-[H^{coupling}]^*$ refers to interaction between occupied→empty and empty→occupied transitions $[(f_{n_2} - f_{n_1}) = -(f_{n_4} - f_{n_3})]$, i.e., it is the coupling between the resonant and the antiresonant part. Resonant and antiresonant blocks

have quite different energies, the former corresponding to positive frequencies and the latter to negative ones, and their coupling is usually neglected. In this way, the two off-diagonal blocks in Eq. (18) are set to zero, the matrix is Hermitian and block-diagonal, and the eigenvalues of the upper block are opposite in sign to the eigenvalues of the lower block. The inversion of $(H^{2p,res} - \omega)$ can be carried out in the spectral form and leads to the final formula for the four point response

$${}^4\chi_{(n_1n_2)(n_3n_4)} = \sum_\lambda \frac{A_\lambda^{(n_1n_2)}\left[A_\lambda^{(n_3n_4)}\right]^*}{E_\lambda - \omega}, \quad (19)$$

where the E_λ and the $A_\lambda^{(n_1n_2)}$ are eigenvalues and eigenvectors of the effective Hamiltonian.
     The eigenvalue problem leading to E_λ and $A_\lambda^{(n_1n_2)}$ has the form of a two-particle equation expressed in the basis of the HFA eigenstates. The first term in the effective Hamiltonian [see Eq. (17)] is the single-particle energy, representing the time evolution of an uncoupled pair. The resonant part of the K term has the following form in the HFA:

$$K_{(vc)(v'c')} = \int u_v^*(x_1)u_c(x_1)v(x_1x_2)u_{v'}(x_2)u_{c'}^*(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 +$$

$$- \int u_v^*(x_1)u_c(x_2)v(x_1x_2)u_{v'}(x_1)u_{c'}^*(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2. \quad (20)$$

The first integral here represents a repulsive interaction which, due to the way indices are coupled, is referred to as the exchange interaction between the electron and the hole. The second integral represents an attractive interaction: this is the electron–hole direct interaction. To avoid confusion, one has to remember that, in spite of its name, the direct term comes from the variation of the single-particle exchange potential in the HFA; in the same way, the exchange interaction between electron and hole is due to the variation of the Hartree potential.

3. Many body perturbation theory

The approach to the two-particle Hamiltonian presented here is only as useful as the underlying HFA. It is known that, especially in solid-state semiconductors, the effects of electronic correlation are not negligible at all. A better approach to the study of ground-state properties is the DFT. In DFT, the non-local exchange potential is substituted with a local exchange-correlation potential: the only physical meaning of this potential is that it reproduces the correct density of the system. However, there is no justification for the interpretation of Kohn–Sham energies as electron addition or removal energies, and the way outlined in the last section for the electron–hole interaction has little meaning in the DFT framework. Only many-body perturbation theory can provide the basis for an interpretation of single-electron wavefunctions in a many-electron system, and for a subsequent justification for the use of single-particle energies and wavefunctions.
     In this section, the Green's function approach is introduced, and the poles of the single-particle Green's function are related to the single-particle properties of the

many-electron system through the quasiparticle concept. The single-particle Hamiltonian which defines the quasi-particles is then obtained in the GW form [7,8] and, following a procedure similar to the one illustrated in the previous section, an effective two-particle Hamiltonian for quasielectron–quasihole interaction is found. Finally, the relationship between the eigenstates and eigenvalues of this Hamiltonian and measurable quantities is shown.

3.1. Second quantization conventions

There is a one-to-one correspondence between normal quantum mechanics in configuration space and the method of second quantization. The reason why the second quantization scheme has surpassed the conventional approach is the ease with which one can treat the many-body problem. In this section the conventions for second quantization are outlined.

The collection of all Slater determinants taken from a complete set of single-particle functions $u_k(x)$ form a complete basis set for any antisimmetric N-particle wavefunction. A notation is introduced in which the determinant is specified by listing the quantum labels $k_1, k_2, \ldots, k_N$. We then have, in this notation,

$$|k_1, k_2, \ldots, k_N\rangle = \frac{\det_{kl}\{u_k(x_l)\}}{\sqrt{N!}}. \tag{21}$$

A creation operator $\hat{c}_k^\dagger$ is defined according to

$$\hat{c}_k^\dagger |k_1, k_2, \ldots, k_N\rangle = |k, k_1, k_2, \ldots, k_N\rangle. \tag{22}$$

The annihilation operator, $\hat{c}_k$, is defined as its Hermitian adjoint. From these definitions, the anticommutation relations are easily obtained

$$\left\{\hat{c}_k^\dagger, \hat{c}_{k'}\right\} = \delta_{kk'}, \qquad \{\hat{c}_k, \hat{c}_{k'}\} = \left\{\hat{c}_k^\dagger, \hat{c}_{k'}^\dagger\right\} = 0. \tag{23}$$

It is convenient to introduce the field operators, $\hat{\psi}(x)$ and $\hat{\psi}^\dagger(x)$, defined as

$$\hat{\psi}(x) = \sum_k \hat{c}_k u_k(x), \qquad \hat{\psi}^\dagger(x) = \sum_k \hat{c}_k^\dagger u_k^*(x). \tag{24}$$

They satisfy the following anticommutation relations

$$\{\hat{\psi}^\dagger(x), \hat{\psi}(x')\} = \delta(xx'), \tag{25a}$$

$$\{\hat{\psi}(x), \hat{\psi}(x')\} = \{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\} = 0. \tag{25b}$$

The creation (annihilation) operator, $\hat{\psi}^\dagger(x)$ [$\hat{\psi}(x)$], adds (destroys) an electron at the point x. If a creation (annihilation) operator acts from the right (left) on the null state the result is 0. The expectation value of the operator $\hat{\rho}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x)$ gives the electron density at the position x, while the operator $\hat{\rho}(xx') = \hat{\psi}^\dagger(x')\hat{\psi}(x)$ corresponds to the density matrix.

The many-body Hamiltonian of the system can be expressed in second quantization in terms of the field operators as

$$\hat{H} = \int h(x)\hat{\psi}^\dagger(x)\hat{\psi}(x)\,\mathrm{d}x + \\ + \frac{1}{2}\int v(xx')\hat{\psi}^\dagger(x)\hat{\psi}^\dagger(x')\hat{\psi}(x')\hat{\psi}(x)\,\mathrm{d}x\,\mathrm{d}x'. \tag{26}$$

Up to now, we have used field operators in the Schrödinger picture. However, one usually prefers to work in the Heisenberg picture where the operators depend on time. In the case of a time-independent Hamiltonian, the relationship between the two pictures is given by $\hat{\psi}(xt) = \mathrm{e}^{\mathrm{i}\hat{H}t}\hat{\psi}(x)\mathrm{e}^{-\mathrm{i}\hat{H}t}$, while for a general Hamiltonian only the derivative of the operator with respect to time is known. The Heisenberg equation of motion is $\mathrm{i}(\partial/\partial t)\hat{\psi}(xt) = [\hat{\psi}(xt), \hat{H}]$. Combining the commutation relations and Eq. (26), it becomes

$$\mathrm{i}\frac{\partial}{\partial t}\hat{\psi}(xt) = \left[h(x) + \int v(xx')\hat{\psi}^\dagger(x't)\hat{\psi}(x't)\,\mathrm{d}x'\right]\hat{\psi}(xt). \tag{27}$$

3.2. One-particle Green's function

We consider a system of N electrons subject to a time-independent Hamiltonian and we define the one-particle Green's function in space coordinates as the expectation value of the Heisenberg field operator in the ground state $|N\rangle$:

$$G(xt, x't') = -\mathrm{i}\langle N|T[\hat{\psi}(xt)\hat{\psi}^\dagger(x't')]|N\rangle. \tag{28}$$

The time-ordered operator T is defined so that the operators are in order of increasing time, reading from right to left, with a sign change for each exchange of fermionic operators:

$$T[\hat{\psi}(xt)\hat{\psi}^\dagger(x't')] = \theta(t - t')\hat{\psi}(xt)\hat{\psi}^\dagger(x't') + \\ - \theta(t' - t)\hat{\psi}^\dagger(x't')\hat{\psi}(xt). \tag{29}$$

Now we introduce the complete set of eigenstates of the many-body Hamiltonian for the $(N + 1)$- and $(N - 1)$-particle states, $|N + 1, s\rangle$ and $|N - 1, s\rangle$, where s denotes the quantum label of each state. By writing $\tau = t - t'$ and keeping in mind that the limiting energy of adding an electron or a hole is the chemical potential μ, we obtain

$$G(xx'\tau) = -\mathrm{i}\sum_s f_s(x)f_s^*(x')\,\mathrm{e}^{-\mathrm{i}\omega_s\tau}\{\theta(\tau)\theta(\omega_s - \mu) + \\ - \theta(-\tau)\theta(\mu - \omega_s)\}. \tag{30}$$

where we have defined the excitation amplitudes and energies as

$$f_s(x) = \langle N|\hat{\psi}(x)|N + 1, s\rangle, \qquad \omega_s = E_{N+1,s} - E_N, \tag{31}$$

for $\omega_s > \mu$, and

$$f_s(x) = \langle N - 1, s|\hat{\psi}(x)|N\rangle, \qquad \omega_s = E_N - E_{N-1,s}, \tag{32}$$

for $\omega_s < \mu$. Now we define the energy representation of the Green's function as a Fourier transform $G(xx'\omega)$

$= \int_{-\infty}^{+\infty} G(xx'\tau)\, e^{i\omega\tau} d\tau$ and obtain

$$G(xx'\omega) = \lim_{\delta \to 0^+} \sum_s \frac{f_s(x)f_s^*(x')}{\omega - \omega_s + i\delta \, \text{sign}(\omega_s - \mu)}. \quad (33)$$

The spectral weight function $A(xx'\omega)$ is introduced as follows:

$$A(xx'\omega) = \sum_s f_s(x)f_s^*(x')\delta(\omega - \omega_s). \quad (34)$$

Consequently the so-called spectral representation of $G(xx'\omega)$ is obtained as

$$G(xx'\omega) = \int_{-\infty}^{+\infty} \frac{A(xx'\omega')}{\omega - \omega'}\, d\omega'. \quad (35)$$

The Green's function and the spectral weight function are here defined in a real space basis: however, an arbitrary basis set can be employed without loss of generality. Let us consider the simple case of free independent fermions with quantum labels k. The Green's function is then a diagonal matrix in k space. The Green's function in energy space is $G_{kk'}(\omega) = \delta_{kk'}[\omega - \omega(k) + i\delta \, \text{sign}\, (\omega_s - \mu)]^{-1}$ and has a pole close to the real axis, while the spectral weight function is simply $A_{kk'} = \delta_{kk'}\delta(\omega - \omega(k))$ and has a very sharp peak at an energy corresponding to the single particle excitation. When the interaction between fermions is introduced, the shape of the spectral weight function can be quite different: however, if the spectral weight function has a peak, we can associate to this peak a so-called quasiparticle excitation, where the peak width is inversely proportional to the lifetime of the excitation. In this case, the Green's function exhibits a pole in the complex plane with a finite imaginary part, which is also inversely proportional to the lifetime of the excitation. The sign of this imaginary part is positive for energies lower than the chemical potential μ (i.e., for holes) and negative for electrons.

The equation of motion for the one-particle Green's function can be obtained by combining its definition and Eq. (27). This leads to the equation

$$\left[i\frac{\partial}{\partial t} - h(x)\right]G(xt, x't') = \delta(xx')\delta(tt') - i\int v(xx'')\times$$

$$\times \langle N|T[\hat{\psi}^\dagger(x''t)\hat{\psi}(x''t)\hat{\psi}(xt)\hat{\psi}^\dagger(x't')]|N\rangle dx''. \quad (36)$$

To simplify the notation, we write $1, 2\ldots$ for (x_1t_1), $(x_2t_2)\ldots$. Now, by defining the two-particle Green's function as

$$G_2(1, 2; 1', 2') = (-i)^2 \langle N|T[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(2')\hat{\psi}^\dagger(1')]|N\rangle, \quad (37)$$

and redefining the instantaneous Coulomb potential as $v(12) = \delta(t_1t_2)v(x_1x_2)$ one can write

$$\left[i\frac{\partial}{\partial t} - h(1)\right]G(1, 1') = \delta(11') - i\int d(2)v(12)G_2(1, 2; 1', 2^+),$$

$$(38)$$

where 2^+ is used here to denote $(x_2t_2^+)$. The two-particle Green's function describes, depending on the time-ordering, the motion of a coupled electron–hole pair, of two electrons, or of two holes. The knowledge of the two-particle Green's function is required to solve the equation of motion for the one-particle Green's function. An infinite chain of coupled equations can be generated, involving Green's functions of higher order. Such a chain can be terminated using a suitable assumption about decoupling. Instead of proceeding in such a way, however, we shall introduce a set of nonlinear equations following the standard field-theoretic procedure.

We define a non-local, time-dependent operator Σ, called the self-energy operator, which is defined by comparing Eq. (36) with the following equation

$$\left[i\frac{\partial}{\partial t} - h(1) - V(1)\right]G(1, 1') - \int d(2)\Sigma(12)G(21') = \delta(11').$$

$$(39)$$

where we have introduced the total average potential defined as $V(x) = \int v(xx')\rho(x')\, dx'$, which is equivalent to the Hartree potential in the HFA. The explicit expression for Σ will be given in the next subsection; for the moment, we only know that it is a non-hermitian operator, that it depends explicitly on time, and that it is a functional of the Green's function. The last equation can be formally simplified by defining the non-interacting Green's function, G_0, through

$$\left[i\frac{\partial}{\partial t} - h(1) - V(1)\right]G_0(1, 1') = \delta(11'). \quad (40)$$

Strictly speaking, this Green's function refers to particles interacting only through the average potential V. Now, the two equations can be combined with $G_0^{-1}G - \Sigma G = 1$, leading to the two following equivalent expressions

$$G^{-1}(12) = G_0^{-1}(12) - \Sigma(12), \quad (41a)$$

$$G(12) = G_0(12) + \int G_0(13)\Sigma(34)G(42)\, d(34). \quad (41b)$$

Going back to the equation of motion, we observe that all quantities in Eq. (39) are functions only of the time differences. We can therefore, take the Fourier transform to obtain

$$[\omega - h(x) - V(x)]G(xx', \omega)+$$

$$- \int \Sigma(xx'', \omega)G(x''x', \omega)\, dx'' = \delta(xx'). \quad (42)$$

We now recall that we are mainly interested in the pole structure of the Green's function, i.e., in the quasiparticle energies. We write the last equation as a matrix product $[\omega - h - V - \Sigma(\omega)]G(\omega) = 1$. A formal solution is then obtained through matrix inversion $G(\omega) = [\omega - h - V - \Sigma(\omega)]^{-1}$. A pole in the Green's function corresponds to a value of ω for which the operator $[\omega - h - V - \Sigma(\omega)]$ is singular, that is its determinant vanishes. In this case, the corresponding homogeneous linear system has a non-trivial

solution

$$[\omega - h(x) - V(x)]u(x,\omega) - \int \Sigma(xx'',\omega)u(x'',\omega) = 0. \qquad (43)$$

The u can be interpreted as the quasiparticle wavefunctions [8]. The equation governing the quasiparticle states is in a certain sense similar to the Hartree–Fock equation: the non-local self-energy operator takes the place of the exchange term, which is also non-local. However, the situation here is more complicated due to the energy dependence and to the non-Hermiticity of the self-energy operator.

3.3. *Hedin's equations and the GW approximation*

Now I will briefly sketch Hedin's approach for deriving an explicit form of the self-energy operator. It is first necessary to observe that the given definition for the Green's function does not apply in the case of a time-dependent Hamiltonian, since the ground state is not well defined. A generalization is possible, but I will not show the details (the reader is invited to refer to the bibliography [5,6]). I merely state the main result, which is an equation that relates the two-particle Green's function to the functional derivative of the single-particle Green's function:

$$\frac{\delta G(11')}{\delta\phi(2)} = -G_2(12,1'2^+) + G(22^+)G(11'). \qquad (44)$$

Here the derivative is taken with respect to both space and time variables.

Using this relation, and with a little algebra, it is possible to arrive at the so-called Hedin's equations.

$$\Sigma(12) = i\int G(13)W(1^+4)\Gamma(324) \, \mathrm{d}(34), \qquad (45a)$$

$$W(12) = v(12) + \int W(13)P(34)v(42) \, \mathrm{d}(34), \qquad (45b)$$

$$P(12) = -i\int G(23)G(42)\Gamma(341) \, \mathrm{d}(34), \qquad (45c)$$

$$\Gamma(123) = \delta(12)\delta(13)+$$
$$+ \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673) \, \mathrm{d}(4567). \qquad (45d)$$

Here, P is the irreducible polarizability, which is equal to the derivative of the charge density with respect to the total potential (here defined as the sum of the external and Hartree potential). The relationship between P and W can be obtaining using the expression for the dielectric response operator $\varepsilon = 1 - vP$ together with the definition of the screened coulomb interaction $W = \varepsilon^{-1}v$. Γ, defined in the last equation, is the so-called vertex function.

These equations, together with the Dyson's equation [Eq. (41)], form a closed set of equations that must in principle be solved self-consistently for G. This means that the Green's function used to calculate the self-energy should be the same as the Green's function obtained from the Dyson equation with the same self-energy. This is a very difficult task, and, in practice, one must find a simplification to Hedin's equations. The simplest approx-

imation to $\Gamma(123)$ assumes that the operator is diagonal in space and time coordinates. $\Gamma(123) = \delta(12)\delta(13)$. That is, it neglects the derivative $\delta\Sigma(12)/\delta G(45)$ in the last equation. The other equations now take the form

$$\Sigma(12) = iG(12)W(1^+2), \qquad (46a)$$

$$W(12) = v(12) + \int W(13)P(34)v(42) \, \mathrm{d}(34), \qquad (46b)$$

$$P(12) = -iG(12)G(21^+). \qquad (46c)$$

This is the GW approximation, so called after the form of the self-energy operator, which is a simple convolution of G and W. The GW approximation has been applied with great success to a wide variety of systems [8,12,13].

It is important to note that Hedin's equations are obtained through an arbitrary but physically meaningful definition of the screened potential W. Similar equations can be obtained by simply replacing W with an appropriate effective interaction. However, due to the fact that these equations are usually solved in a perturbative way (i.e., not in a fully self-consistent fashion), a better effective interaction leads to faster convergence. For example, if the bare Coulomb potential was used instead of the screened one, we would obtain a set of equations whose first interaction lead to the HFA, and, with an iterative procedure, one could obtain the correct result. This procedure is used in calculations for atoms or small molecules, were the polarizability is small and the screening is not very efficient. However, in systems with high polarizability and dielectric constant much greater than unity, such as bulk semiconductors, the screening is not negligible and the GW approach leads to a much faster convergence.

3.4. *The Bethe–Salpeter equation for the irreducible polarizability*

The solution of Hedin's equation leads to an exact determination of the polarizabiliy P and thus of the dielectric constant. However, a different procedure can be employed, that leads to a physically sounder two-particle equation similar to the one already obtained in Section 2.3.

To update the vertex equation in a second iteration we need to know the form of the derivative of the self energy with respect to the Green's function. Here we take $\delta\Sigma/\delta G = iW$, using the GW expression for the self-energy, and neglecting the term $iG(\delta W/\delta G)$, which is usually considered small [14,15]. The resulting vertex equation is

$$\Gamma(123) = \delta(12)\delta(13) - iW(1^+2)\int G(46)G(75)\Gamma(673) \, \mathrm{d}(4567).$$

$$(47)$$

The polarizability P is a two-point function because the perturbation is in the form of a local potential and we are interested in the local part of the resulting charge variation. However, to obtain an equation similar to Eq. (17) we need four-point quantities. We generalize to a three-point

polarizability defined as

$$^3P(312) = -\mathrm{i}\int G(16)G(72)\Gamma(671)\,\mathrm{d}(67) \qquad (48)$$

and obtain the following equation

$$^3P(345) = -\mathrm{i}G(43)G(35) + \mathrm{i}\int G(41)G(25)W(1^+2)\,^3P(312). \qquad (49)$$

The two-point polarizability can be obtained from the three-point polarizability using $P(12) = {}^3P(122)$. However, we further generalize to four point quantities and, defining the independent quasiparticle response $\chi_0(1234) = -\mathrm{i}G(14)G(32)$, and extending to a four point screened potential $^4W(1234) = W(1^+2)\delta(13)\delta(24)$, we obtain the following expression for a generalized four-point polarizability

$$^4P(1234) = {}^4\chi_0(1234) +$$
$$- \int {}^4\chi_0(1256)\,^4W(5678)\,^4P(7834)\,\mathrm{d}(5678). \qquad (50)$$

This equation is called the Bethe–Salpeter equation (BSE) for the four-point polarizability, and is very similar to Eq. (10). However, in this case the integrals are extended over time and space variables. Moreover, only an attractive component appears, and it is screened. We will see in the following subsections how to obtain the repulsive part of the interaction. Note that we need only the two point polarizability for the local response to a local potential. It can be obtained by contracting the four point polarizability in the form $P(12) = {}^4P(1221)$.

3.5. Connection to macroscopic properties

The BSE equation is usually employed to obtain absorption and sometimes energy-loss spectra. The absorbtion is proportional to the imaginary part of the macroscopic dielectric tensor. However, the relationship between macroscopic and microscopic functions is not trivial. I have shown in the previous subsection that the irreducible polarizability is related to dielectric response through the relation $\varepsilon = 1 - vP$. The total potential is then obtained from $\varepsilon V_{\mathrm{tot}} = V_{\mathrm{ext}}$, giving $V_{\mathrm{tot}} = \varepsilon^{-1}V_{\mathrm{ext}}$. Here ε is a matrix and ε^{-1} is obtained by matrix inversion. If we go over to reciprocal space and define the spatial Fourier components of a two point quantity $S(x_1x_2)$ as

$$S_{GG'}(q) = \int \mathrm{e}^{\mathrm{i}(G+q)\cdot x_1} S(x_1x_2)\,\mathrm{e}^{-\mathrm{i}(G'+q)\cdot x_1}\,\mathrm{d}x_1\,\mathrm{d}x_2, \qquad (51)$$

the macroscopic value of S is the $S_{00}(0)$ term. If we apply an external macroscopic potential, the induced total potential is in general non-macroscopic and has the following form in reciprocal space:

$$V_{\mathrm{tot}}(G+q) = \varepsilon_{G0}^{-1}(q)V_{\mathrm{ext}}(q). \qquad (52)$$

Even if we are only interested in the macroscopic component of the induced potential, we have to compute

the element $\varepsilon_{00}^{-1}(0)$, which depends on the full matrix $\varepsilon_{GG'}(0)$. The reason is that the system responds to the perturbation with a microscopic change in the density, and all the details of this variation affect the electronic structure of the perturbed state. The macroscopic dielectric response which relates $V_{\mathrm{tot}}(0)$ and $V_{\mathrm{ext}}(0)$ is calculated using the expression

$$\varepsilon_M(\omega) = \frac{1}{\varepsilon_{G=0,G'=0}^{-1}(q=0)}. \qquad (53)$$

It is possible to show (see Appendix II) that the relationship between the macroscopic dielectric response and the polarization P can be written as

$$\varepsilon_M(\omega) = 1 - \lim_{q\to 0} v(q)\bar{P}_{00}(q) \qquad (54)$$

where $\bar{P}$ is a modified polarizability which is related to the polarizability P through a Dyson-like equation

$$\bar{P} = P + P\bar{v}\bar{P}. \qquad (55)$$

In the last equation, $\bar{v}$ is the Coulomb potential minus the long-range tail [see Eq. (II4)]. The limit $q \to 0$ has to be taken because of the divergence of the coulomb potential in the $q \to 0$ limit. It is also interesting to note that, in the same way, the macroscopic component of the inverse dielectric response $\varepsilon_{00}^{-1}(0)$ can be written as

$$\varepsilon_{00}^{-1}(0) = 1 + \lim_{q\to 0} v(q)\chi_{00}(q), \qquad (56)$$

where the Dyson equation defining the total response χ is

$$\chi = P + Pv\chi. \qquad (57)$$

The only difference between Eqs. (55) and (57) is in the tail of the Coulomb potential.

The point here is that, if we wish to calculate the macroscopic dielectric function $\varepsilon_M(\omega)$ to compute the optical absorption, then we have to calculate the modified polarizability $\bar{P}$. If we are interested in the inverse dielectric function (e.g., for the calculation of loss spectra) then we need the response function χ.

3.6. Bethe–Salpeter equation in practice

Now, extending Eqs. (55) and (57) to their four-point form, and substituting in the BSE for the polarizability [Eq. (50)] we obtain the BSE equation for the modified polarizability and for the response function, respectively

$$^4\bar{P} = {}^4\chi_0 + {}^4\chi_0(^4\bar{v} - {}^4W)^4\bar{P}, \qquad (58a)$$

$$^4\chi = {}^4\chi_0 + {}^4\chi_0(^4v - {}^4W)^4\chi. \qquad (58b)$$

These equations are very similar to Eq. (10). Some observation are now required

- The attractive part of the kernel $^4W(1234) = W(12)\delta(13)\delta(24)$ is now the screened Coulomb potential which is in general a complex energy-dependent two-point function, which comes from the variation of the self-energy. The repulsive part includes the long-range tail, if we are interested in the inverse of the dielectric

function, and omits it, if we aim to calculate the optical absorption.

- The repulsive, bare interaction arises from the definition of the polarizability, *P*. If one writes Hedin's equation in a form where the Hartree potential is treated together with the self-energy, it is possible to show that the repulsive interaction comes from the variation of the Hartree potential. This is the reason why it is not screened. The lack of long-range exchange effects is related to the inversion of the ε matrix.

At this point another approximation is usually introduced: the energy dependence of the screened potential is neglected and one assumes $W(\omega) = W(\omega = 0)$. With this simplification, the form of Eqs. (10) and (58) is exacly the same, and the approach used in Section 2.3 to obtain the two-particle Hamiltonian can be used here as well. Dynamical effects on the screened potential have been studied in Ref. [16]. A general rule is that they can be neglected when the exciton binding energy is smaller than the plasma frequency [17].

In its final form, the BSE equation is an eigenvalue problem

$$\sum_{n_3 n_4} \{(\omega_{n_1} - \omega_{n_2})\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2})[\bar{v}_{(n_1 n_2)(n_3 n_4)} +$$

$$- W_{(n_1 n_2)(n_3 n_4)}]\}A_\lambda^{(n_3 n_4)} = E_\lambda A_\lambda^{(n_1 n_2)}, \qquad (59)$$

where the matrix elements are expressed in a basis of one-particle orbitals. Here the coupling between the resonant and the antiresonant parts are usually neglected (see Section 2.3). This approximation is often referred to as the Tamm–Dancoff approximation [6], and is discussed in Refs. [18] and [19]. Once the matrix is diagonalized, the macroscopic dielectric constant can be calculated using the following expression

$$\varepsilon_M(\omega) = 1 - \lim_{q \to 0} v(q) \sum_\lambda \frac{|\sum_{n_1 n_2} \langle n_1 | e^{iq \cdot r} | n_2 \rangle A_\lambda^{(n_1 n_2)}|^2}{\omega - E_\lambda + i\delta}. \qquad (60)$$

A similar equation is obtained for the macroscopic component of ε^{-1}.

Another important point is that the spin degree of freedom is usually neglected in the BSE. Since the effective Hamiltonian conserves the spin, the two-particle states can be classified as singlets (total spin equal to zero) and triplets (total spin equal to one). Only the first class of states are involved in optical transitions. After the Hamiltonian is reduced in block form, two different Hamiltonians are obtained for singlet and triplet states: in the latter, there is no exchange term $\bar{v}$, while in the former, the exchange term is included with a factor of two.

Finally, in periodic systems, the effective Hamiltonian also conserves the lattice momentum. Only states with zero total momentum contribute to the macroscopic dielectric constant. Therefore, vertical transitions (those conserving *k*) are mixed.

A number of quantities can be calculated from the eigenstates and eigenvalues of the BSE. First of all, as we have already seen, the imaginary part of the macroscopic dielectric constant, which is proportional to the absorption

cross section, can be calculated. Moreover, an effective electron–hole wavefunction can be obtained as

$$\Psi_{eh}^\lambda(r_e, r_h) = \sum_\lambda A_\lambda^{(cv)} u_c(r_e) u_v^*(r_h). \qquad (61)$$

Since the many-body structure of the excited state wavefunction is complex, this is not an exact relationship. However, it can give visual information as to the average value of the electron–hole distance, if one fixes the position of one of the two effective particles on an arbitrary point and plots the probability density of finding the other particle as a function of relative position.

A final consideration has to be made. In the case of periodic systems, the states are labelled by a band index and a *k* vector. The dimension of the Bethe–Salpeter matrix is equal to $(N_c N_v N_k)^2$, where N_c and N_v are the number of conduction and valence bands included in the calculation, and N_k is the number of special points used to discretize the Brillouin zone. The ratio of the diagonal elements of the interaction kernels to the diagonal part due to quasi-particle transitions tends to 0 when $N_k \to \infty$, due to normalization factors. Therefore, it is not possible to use the BSE in a perturbative way by simple inspection of the diagonal elements. On the other hand, if the system is finite or, equivalently, a finite k-mesh is used (and this is always the case in practice), the interaction kernel also acts on the diagonal part and gives a perturbative shift. However, in the case of infinite systems, this is a spurious effect, and what actually happens is that there is no red-shift due to the electron–hole interaction. The only effect of the interaction is the eventual appearence of discrete bound states (excitons), observed as strong peaks in the absorption spectrum, and a modification of the absorption strength corresponding to unbound states.

4. Applications

In practical applications, the following scheme is typically followed:

- A ground state self-consistent DFT calculation (usually LDA) in which the Kohn–Sham eigenstates and energies are obtained.
- The independent-particle response function χ_0 is calculated from Kohn–Sham states. The ε^{-1} is obtained through $\varepsilon^{-1} = (1 - v\chi_0)^{-1}$. This corresponds to a consideration of only the exchange interaction (coming from the Hartree potential) between fictitious Kohn–Sham particles. The static W is then calculated.
- The self-energy is obtained in the GW approximation by combining the *G* and the *W* obtained from Kohn–Sham states. The GW energy is subsequently calculated for each Kohn–Sham state. In this step, the GW quasi-particle wavefunction is usually taken to be equal to the KS wavefunctions. A discussion of this assumption can be found in Ref. [16].
- Starting from the Kohn–Ssam wavefunctions, the GW energies and the already obtained *W*, the Bethe–Salpeter matrix is constructed and diagonalized.
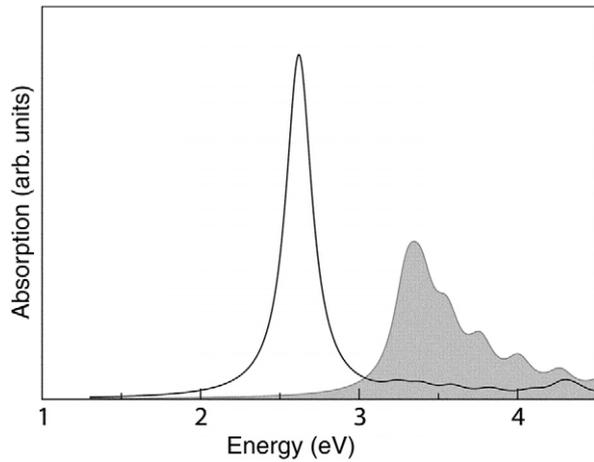- Equation (60) is used to calculate the absorption spectrum.

Fig. 1. The calculated absorption spectrum for PPV is shown [23]. The shaded line represents the absorption obtained arbitrarily switching off the electron–hole interaction: a $1/\sqrt{E}$ peak is observed, corresponding to the band gap. The dark line is obtained including electron–hole interaction: the absorption at the band gap is strongly suppressed, and a peak due to a bound exciton arises at lower energy.

Various examples of the possibility of obtaining realistic absorption spectra through the BSE can be found in the literature [9,20–22]. Bulk silicon is probably one of the most studied systems. In the case of Si, the dielectric screening is quite large, and no bound exciton is observed in the absorption spectrum. However, the spectrum predicted neglecting the electron–hole interaction kernel is quite different from the experimental one. When the electron–hole interaction is introduced, the shape of the simulated spectrum comes very close to experiment. The reader can refer to the indicated bibliography for a discussion of the various degrees of approximation. As a short guide, the most widely-used methods used are listed and described below:

- DFT-RPA: in this case, the transitions between independent Kohn–Sham states are considered, and no electron–hole interaction is introduced. The onset for the absorption is the Kohn–Sham gap, which is usually smaller than the experimental optical gap.

- GW-RPA: here the transitions are between independent quasi-particle states. In this case, the optical gap is usually larger than the experimental one.
- GW-LFE: here, the local field effects are included, that is only the exchange part of the electron–hole interaction is considered. In this case $P = \chi_0$, there is no need for a two-particle Hamiltonian and Eq. (55) is directly inverted.
- BSE: this is the full BSE, where both screened and bare interaction are included.

The case of low-dimensional systems, where dimensionality effects are critical, is even more interesting, due to the formation of bound excitons. As an example, the absorption spectrum of a typical one-dimensional polymer, polypara-phenylenevinylene (PPV), is calculated in Ref. [23]. In this work, the results for the non-interacting and interacting electron–hole pairs (in the above list, GW-RPA and BSE) are compared for a PPV chain. In the non-interacting case a strong $1/\sqrt{E}$ peak in the absorption spectrum (see Fig. 1) at an energy corresponding to the valence-conduction band gap is obtained due to the one-dimensional Van Hove singularity in the joint density of states. When the electron–hole interaction is turned on, a discrete bound exciton appears at an energy lower than the band gap and the Van Hove singularity is suppressed. This leads to an apparent red shift of the lowest peak. However, it turns out that the unbound states are not shifted, and the suppression of the Van Hove singularity is related to an orthonormalization of the unbound states with the bound exciton, which indeed has a very large oscillator strength due to strong electron–hole localization. Similar results have been obtained by different groups for other polymers [24–26].

The case of crystalline polymers, which are made up of a collection of polymer chains, is also interesting. In this case, the system is three-dimensional, but retains partially quasi-one-dimensional properties of an isolated polymer. The excitonic properties are modified by the interchain coupling: as an example, in calculations for crystalline PPV [23] and polythiophene [27] the two-particle excitonic wavefunction (see Fig. 2) can be used to distinguish between direct excitons (electron and hole on the same
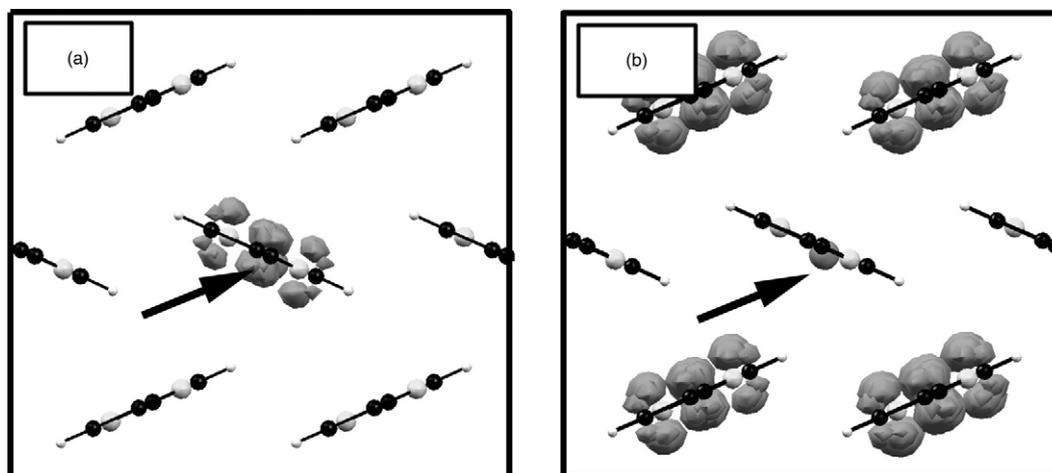

Fig. 2. Excitonic wavefunction for (a) direct and (b) charge-transfer states in PT [27]. The hole is fixed in the position indicated by the arrow, and the probability of finding the electron is plotted.

chain) and charge-transfer excitons (electron and hole on different chains). In both cases, bound charge-transfer states are found at energies just above the lowest direct exciton.

5. Summary

In these notes, the effects of electron–hole interaction on the optical properties of materials have been discussed on different levels of approximation. The most accurate method for including them is the Bethe–Salpeter equation, which we have just derived. However, the discussion outlined here is far from complete, and the reader is invited to refer to the bibliography for a more detailed discussion.

Acknowledgments

Appendix I: Independent-particle polarizability

In this appendix one possible derivation of the independent-particle response is sketched. One assumes that a collection of independent fermions is subject to a possibly non-local Hamiltonian $H(xx't)$ made up of a static part $H^{(0)}(xx')$ and a dynamic perturbation $V(xx't)$. The unperturbed Hamiltonian leads to a time-independent Schrödinger equation,

$$\int H^{(0)}(xx')u_k(x')\,\mathrm{d}x' = \omega_k u_k(x), \tag{I1}$$

with eigenvalues ω_k and eigenvectors $u_k(x)$. The $u(x)$ can be used as a basis set for a generic non-local operator S. We have then $S(xx') = \sum_k u_k^*(x)u_{k'}(x')S_{kk'}$. In this basis, the $H^{(0)}$ and V operators read

$$H_{kk'}^{(0)} = \omega_k \delta_{kk'}, \tag{I2a}$$

$$V_{kk'}(t) = \int u_k(x)V(xx't)u_{k'}^*(x')\,\mathrm{d}x\,\mathrm{d}x'. \tag{I2b}$$

The time-dependent problem involving the total Hamiltonian H has solutions described by the Schrödinger equation

$$\mathrm{i}\frac{\partial}{\partial t}u_k(xt) = \int H(xx't)u_k(x't)\,\mathrm{d}x'. \tag{I3}$$

One also consider the density matrix, defined as

$$\rho(xx't) = \sum_k f_k u_k^*(x't)u_k(xt). \tag{I4}$$

In the unperturbed problem, the density matrix expressed on the basis of the static eigenvectors, is simply $\rho_{kk'}^{(0)} = f_k\delta_{kk'}$. In the time-dependent case, the equation of motion for the density matrix is found using Eq. (I3), and

the final result is

$$\mathrm{i}\frac{\partial}{\partial t}\rho_{kk'}(t) = \sum_l [H_{kl}(t)\rho_{lk'}(t) - \rho_{kl}(t)H_{lk'}(t)]. \tag{I5}$$

Now, keeping only the linear correction to the density matrix, and defining $\rho^{(1)}$ through the equation $\rho = \rho^{(0)} + \rho^{(1)}$, one obtains

$$\mathrm{i}\frac{\partial}{\partial t}\rho_{kk'}^{(1)}(t) = (\omega_k - \omega_{k'})\rho_{kk'}^{(1)}(t) + (f_{k'} - f_k)V_{kk'}(t). \tag{I6}$$

Going over to frequency space, the expression for $\rho^{(1)}$ is

$$\rho_{kk'}^{(1)}(\omega) = \frac{f_k - f_{k'}}{\omega_k - \omega_{k'} - \omega}V_{kk'}(\omega). \tag{I7}$$

The expression of the independent-particle polarizability, which is defined as the functional derivative of the density matrix with respect to the perturbing potential, is then, on this basis

$$\frac{\delta\rho_{kk'}}{\delta V_{k''k'''}} = \frac{f_k - f_{k'}}{\omega_k - \omega_{k'} - \omega}\delta_{kk''}\delta_{k'k''}. \tag{I8}$$

Appendix II: Long-range tail of the Coulomb interaction

In this appendix the demonstration of Eq. (54) is outlined. The definition of the microscopic inverse dielectric constant in term of the irreducible polarizability is $\varepsilon^{-1} = (1 - vP)^{-1}$. A matrix inversion is required, but only one element (the macroscopic part) of the result is needed. If a is a scalar, $\underline{b}$ and $\underline{c}$ are vectors and D is a matrix, the following relationship holds

$$\begin{pmatrix} a & \underline{b}^T \\ \underline{c} & D \end{pmatrix}^{-1} = \begin{pmatrix} 0 & 0 \\ 0 & D^{-1} \end{pmatrix} + \frac{1}{a - \underline{b}^T D^{-1}\underline{c}} \times$$
$$\times \begin{pmatrix} 1 & -\underline{b}^T D^{-1} \\ -D^{-1}\underline{c} & D^{-1}\underline{c}\underline{b}^T D^{-1} \end{pmatrix} \tag{II1}$$

which can be verified by substitution. Now the dielectric response is defined as $\varepsilon = 1 - vP$ which in block form reads

$$\varepsilon = \begin{pmatrix} 1 - v(q)P_{00}(q) & -v(q)P_{0G'}(q) \\ -v(G+q)P_{G0}(q) & \delta_{GG'} - v(G+q)P_{GG'}(q) \end{pmatrix}$$
$$= \begin{pmatrix} 1 - v(q)P_{00}(q) & -v(q)P_{0G'}(q) \\ -v(G+q)P_{G0}(q) & \check{\varepsilon}_{GG'}(q) \end{pmatrix} \tag{II2}$$

which defines $\check{\varepsilon}_{GG'}(q)$. Using Eq. (II1), one obtains

$$\frac{1}{\varepsilon_{00}^{-1}(q)} = 1 - v(q)P_{00}(q) + \sum_{GG'} v(q)P_{0G}(q)\check{\varepsilon}_{GG'}^{-1}v(G'+q)P_{G'0}(q). \tag{II3}$$

On the other hand, Eq. (55) can be inverted to obtain $\bar{P} = (1 - P\bar{v})^{-1}P$. In block form, defining the $\bar{v}$ potential as

$$\bar{v}(q+G) = \begin{cases} 0 & \text{if } G = 0, \\ v(q+G) & \text{if } G \neq 0, \end{cases} \tag{II4}$$

one writes

$$1 - P\bar{v} = \begin{pmatrix} 1 & P_{0G'}(q)v(G'+q) \\ 0 & \check{\varepsilon}_{G'G}(q) \end{pmatrix}. \tag{II5}$$

The presence of a null block simplifies the matrix inversion. As a special case of Eq. (II1), one has

$$\begin{pmatrix} 1 & \underline{b}^T \\ 0 & D \end{pmatrix}^{-1} = \begin{pmatrix} 1 & -\underline{b}^T D^{-1} \\ 0 & D^{-1} \end{pmatrix}. \tag{II6}$$

This leads to the following expression for the modified polarization

$$(1 - P\bar{v})^{-1} = \begin{pmatrix} 1 & \sum_{G''} P_{0G''}(q)v(G''+q)\check{\varepsilon}_{G'G''}^{-1}(q) \\ 0 & \check{\varepsilon}_{G'G}^{-1}(q) \end{pmatrix}.$$

Proceeding in this way, one finds the expression for $\bar{P}_{00}(q)$, which reads

$$\bar{P}_{00}(q) = P_{00}(q) - \sum_{GG'} P_{0G}(q)v(q+G)\check{\varepsilon}_{G'G}^{-1}(q)P_{G'0}(q). \tag{II8}$$

Finally, the value of $1 - v(q)\bar{P}_{00}(q)$ is found to be equivalent to the expression $1/\varepsilon_{00}^{-1}(q)$ given in Eq. (II3).

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