

9. Models of Excitons

At this point, one might wonder about the accuracy of the optical response calculated in the previous chapters. So far, we have been treating the electrons as independent particles and the question is to what extent this is sufficient. For bulk semiconductors, the single-particle calculations predict an absorption edge that is essentially a square root, c.f. Fig. 8.1. As a classic example of the failure of this prediction, Fig. 9.1 shows a comparison between experimental spectra [1] and theoretical single-particle spectra computed from Eq.(7.4) for the wurtzite semiconductor ZnO.

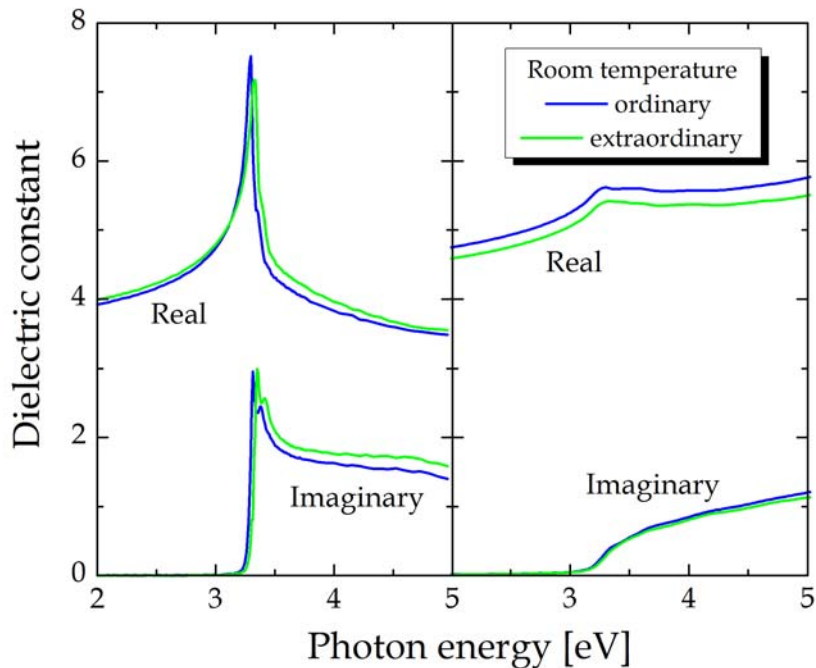


Figure 9.1 Measured spectra (left panel) and calculated single-particle spectra (right panel) for ZnO. The ordinary and extraordinary spectra correspond to light polarized perpendicular and parallel to the crystal c -axis, respectively.

It is obvious that single-particle theory fails miserably in this case. In most materials, however, the discrepancy is less pronounced but still noticeable. The aim of this chapter is to describe a method for the inclusion of effects beyond the single-particle response. It involves a much more accurate calculation of many-body excited states usually referred to as excitons. In subsequent chapters, the effects of excitons in low-dimensional semiconductors will be investigated. We will demonstrate that excitons are even more important for those cases.

Applying the single-particle approximation means, in effect, approximating all-electron wave functions by Slater determinants. To demonstrate this fact, we turn to the more general expression for the optical susceptibility

$$\chi(\omega) = \frac{2e^2\hbar^2}{\varepsilon_0 m^2 \Omega} \sum_{exc} \frac{\left| \langle 0 | \hat{P}_z | exc \rangle \right|^2}{E_{exc} [E_{exc}^2 - \hbar^2(\omega + i\Gamma)^2]}$$

This expression differs from the single-particle result Eq.(7.4) in that the sum is over all excited states $|exc\rangle$ with excitation energy E_{exc} , i.e. energy measured relative to the ground state $|0\rangle$. The prefactor of 2 (rather than 4) is used because the summation also covers spin. Also, the operator \hat{P}_z is the many-body momentum operator, which for a system with $2N$ electrons is given as the sum of single-electron operators

$$\hat{P}_z = \sum_{n=1}^{2N} \hat{p}_{z,n},$$

where $\hat{p}_{z,n} = -i\hbar d/dz_n$ operates on the n 'th electron coordinate only. The ground state is a Slater determinant

$$|0\rangle = |(v_{1\uparrow}), (v_{1\downarrow}), \dots, (v_{N\uparrow}), (v_{N\downarrow})|$$

with all single-electron valence states occupied by spin-up and -down electrons. The total spin of the ground state is zero and since optical excitations don't flip spins we look for excited states with vanishing spin. These are so-called singlet states. To construct them, we first examine two types of singly-excited states

$$\begin{aligned} |(v_{i\uparrow}) \rightarrow (c_{j\uparrow})\rangle &= |\dots, (c_{j\uparrow}), (v_{i\downarrow}), \dots\rangle \\ |(v_{i\downarrow}) \rightarrow (c_{j\downarrow})\rangle &= |\dots, (v_{i\uparrow}), (c_{j\downarrow}), \dots\rangle \end{aligned}$$

in which a single occupied spin-up or -down orbital is replaced by unoccupied (conduction) states with similar spin. Neither of these states have definite *total* spin. However, the combination $|v_i \rightarrow c_j\rangle \equiv \{ |(v_{i\uparrow}) \rightarrow (c_{j\uparrow})\rangle + |(v_{i\downarrow}) \rightarrow (c_{j\downarrow})\rangle \} / \sqrt{2}$ is a singlet with total spin $S = 0$. We now use the rules for matrix elements between Slater determinants [2] to calculate for the momentum

$$\langle 0 | \hat{P}_z | v_i \rightarrow c_j \rangle = \sqrt{2} \langle v_i | \hat{p}_z | c_j \rangle.$$

Moreover, the energy difference between the singlet and the ground state is simply $E_{c_j} - E_{v_i}$. Hence, Eq.(9.1) reduces exactly to Eq.(7.4) in this case.

We now wish to be somewhat more accurate. To this end, we write the excited states as linear combinations of the singlets above, i.e.

$$|exc\rangle = \sum_{ij} \Psi_{ij} |v_i \rightarrow c_j\rangle,$$

where Ψ_{ij} are unknown expansion factors. The problem is how to find matrix elements of the total Hamiltonian for any two singlets

$$H_{ij,kl} = \langle v_i \rightarrow c_j | \hat{H} | v_k \rightarrow c_l \rangle.$$

The total Hamiltonian is given by

$$\hat{H} = \sum_{n=1}^{2N} \hat{h}_n + \sum_{n<m}^{2N} V(\vec{r}_n - \vec{r}_m), \quad V(\vec{r}) = \frac{e^2}{4\pi\epsilon_0 r},$$

where \hat{h}_n is the single-electron Hamiltonian. As a start we look at the energy of the ground state

$$\langle 0 | \hat{H} | 0 \rangle = 2 \sum_{n=1}^N \langle v_n | \hat{h} | v_n \rangle + \sum_{n,m}^N \{ 2 \langle v_n v_m | V | v_n v_m \rangle - \langle v_n v_m | V | v_m v_n \rangle \}.$$

Note that the additional factors of 2 appear because the spin-summation has already been performed. Next, we look at the diagonal elements for the state $|(v_i \uparrow) \rightarrow (c_j \uparrow)\rangle$. Compared to the ground state, v_i should be replaced by c_j . It follows that

$$\begin{aligned} \langle (v_i \uparrow) \rightarrow (c_j \uparrow) | \hat{H} | (v_i \uparrow) \rightarrow (c_j \uparrow) \rangle &= \langle 0 | \hat{H} | 0 \rangle + \langle c_j | \hat{h} | c_j \rangle - \langle v_i | \hat{h} | v_i \rangle \\ &+ \sum_{n \neq i} \{ 2 \langle v_n c_j | V | v_n c_j \rangle - \langle v_n c_j | V | c_j v_n \rangle \} + \langle v_i c_j | V | v_i c_j \rangle - \sum_n \{ 2 \langle v_n v_i | V | v_n v_i \rangle - \langle v_n v_i | V | v_i v_n \rangle \}. \end{aligned}$$

We now introduce the *quasi-particle* energies

$$\begin{aligned} \tilde{E}_{c_j} &\equiv \langle c_j | \hat{h} | c_j \rangle + \sum_{n=1}^N \{ 2 \langle v_n c_j | V | v_n c_j \rangle - \langle v_n c_j | V | c_j v_n \rangle \} \\ \tilde{E}_{v_i} &\equiv \langle v_i | \hat{h} | v_i \rangle + \sum_{n=1}^N \{ 2 \langle v_n v_i | V | v_n v_i \rangle - \langle v_n v_i | V | v_i v_n \rangle \}. \end{aligned}$$

Note that there is no restriction on the summations, i.e. all valence states are summed. In terms of these quantities we have

$$\langle (v_i \uparrow) \rightarrow (c_j \uparrow) | \hat{H} | (v_i \uparrow) \rightarrow (c_j \uparrow) \rangle = \langle 0 | \hat{H} | 0 \rangle + \tilde{E}_{c_j} - \tilde{E}_{v_i} - \langle v_i c_j | V | v_i c_j \rangle + \langle v_i c_j | V | c_j v_i \rangle,$$

where the last two terms serve to correct the unrestricted summations in the quasi-particle energies. The exact same expression is obtained if the spin-down Slater determinant is considered. The cross-term yields

$$\langle (v_i \uparrow) \rightarrow (c_j \uparrow) | \hat{H} | (v_i \downarrow) \rightarrow (c_j \downarrow) \rangle = \langle v_i c_j | V | c_j v_i \rangle.$$

Combining, we find the full diagonal matrix element for the singlet excitation

$$\langle v_i \rightarrow c_j | \hat{H} | v_i \rightarrow c_j \rangle = \langle 0 | \hat{H} | 0 \rangle + \tilde{E}_{c_j} - \tilde{E}_{v_i} - \langle v_i c_j | V | v_i c_j \rangle + 2 \langle v_i c_j | V | c_j v_i \rangle.$$

It can be shown that coupling between singly excited states and the ground state is identically zero, i.e. that $\langle 0 | \hat{H} | v_i \rightarrow c_j \rangle = 0$ [3]. The non-zero off-diagonal terms follow in much the same style as the diagonal ones

$$\begin{aligned} \langle (v_i \uparrow) \rightarrow (c_j \uparrow) | \hat{H} | (v_k \uparrow) \rightarrow (c_l \uparrow) \rangle &= \langle c_j v_k | V | v_i c_l \rangle - \langle c_j v_k | V | c_l v_i \rangle \\ \langle (v_i \uparrow) \rightarrow (c_j \uparrow) | \hat{H} | (v_k \downarrow) \rightarrow (c_l \downarrow) \rangle &= \langle c_j v_k | V | v_i c_l \rangle. \end{aligned}$$

As $\langle 0 | \hat{H} | 0 \rangle$ is the ground state energy, which we use as a zero-point of energy, we finally find

$$H_{ij,kl} = [\tilde{E}_{c_j} - \tilde{E}_{v_i}] \delta_{ik} \delta_{jl} - \langle c_j v_k | V | c_l v_i \rangle + 2 \langle c_j v_k | V | v_i c_l \rangle. \quad (9.1)$$

The matrix problem then reads as

$$\sum_{kl} H_{ij,kl} \Psi_{kl} = E_{exc} \Psi_{ij},$$

from which exciton wave functions and energies are computed. In turn, the exciton momentum matrix elements become

$$\langle 0 | \hat{P}_z | exc \rangle = \sqrt{2} \sum_{ij} \Psi_{ij} \langle v_i | \hat{p}_z | c_j \rangle. \quad (9.2)$$

We now specialize to periodic solids for which orbitals are labeled by a band index (v or c) and a wave vector \vec{k} . In an optical process, the only relevant excitations are those that preserve \vec{k} (neglecting the small momentum lost/gained by the photon). Thus, the singlets are of the type $|v\vec{k}\rangle \equiv |v\vec{k} \rightarrow c\vec{k}\rangle$. In turn, the sought matrix elements are

$$H_{v\vec{k},v'c'\vec{k}'} = [\tilde{E}_{c\vec{k}} - \tilde{E}_{v\vec{k}}] \delta_{vv'} \delta_{cc'} \delta_{\vec{k}\vec{k}'} - \langle v\vec{k} | V_C | v'c'\vec{k}' \rangle + 2 \langle v\vec{k} | V_x | v'c'\vec{k}' \rangle, \quad (9.3)$$

where Coulomb and exchange matrix elements are defined as

$$\begin{aligned}\langle v\vec{c}\vec{k} | V_C | v'c'\vec{k}' \rangle &= \iint \psi_{c\vec{k}}^*(\vec{r})\psi_{c'\vec{k}'}(\vec{r})V(\vec{r}-\vec{r}')\psi_{v\vec{k}}(\vec{r}')\psi_{v'\vec{k}'}^*(\vec{r}')d^3rd^3r' \\ \langle v\vec{c}\vec{k} | V_x | v'c'\vec{k}' \rangle &= \iint \psi_{c\vec{k}}^*(\vec{r})\psi_{c'\vec{k}'}(\vec{r}')V(\vec{r}-\vec{r}')\psi_{v\vec{k}}(\vec{r})\psi_{v'\vec{k}'}^*(\vec{r}')d^3rd^3r'.\end{aligned}$$

In a more rigorous derivation [4], it turns out that the Coulomb interaction should be screened by surrounding charges, so that introducing the dielectric constant ε we find

$$\langle v\vec{c}\vec{k} | V_C | v'c'\vec{k}' \rangle = \frac{1}{\varepsilon} \iint \psi_{c\vec{k}}^*(\vec{r})\psi_{c'\vec{k}'}(\vec{r})V(\vec{r}-\vec{r}')\psi_{v\vec{k}}(\vec{r}')\psi_{v'\vec{k}'}^*(\vec{r}')d^3rd^3r'.$$

This full matrix equation (using the screened Coulomb interaction) is known as the Bethe-Salpeter equation.

9.1 Wannier model

The framework above is terribly complicated and extremely difficult to handle numerically. Fortunately, a much simplified version can be applied in many cases provided the Coulomb interaction is not too strong. To derive this “Wannier” model we first note that the eigenstates of a periodic solid can be written as

$$\psi_{v\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} u_{v\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}},$$

where $u_{v\vec{k}}$ is the lattice-periodic part normalized so that

$$\frac{1}{\Omega_{UC}} \int_{UC} |u_{v\vec{k}}(\vec{r})|^2 = 1$$

with the integral taken over the unit cell volume Ω_{UC} . We first turn to the Coulomb matrix element. The product $\psi_{v\vec{k}}(\vec{r}')\psi_{v'\vec{k}'}^*(\vec{r}')V(\vec{r}-\vec{r}')$ has a rapidly varying periodic part and slow part. In analogy with chapter 7, we will approximate the integral

$$\begin{aligned}\int \psi_{v\vec{k}}(\vec{r}')\psi_{v'\vec{k}'}^*(\vec{r}')V(\vec{r}-\vec{r}')d^3r' &\approx \frac{1}{\Omega_{UC}} \int u_{v\vec{k}}(\vec{r}')u_{v'\vec{k}'}^*(\vec{r}')d^3r' \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'}V(\vec{r}-\vec{r}')d^3r' \\ &\equiv \frac{1}{\Omega} I_{v'\vec{k}',v\vec{k}} \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'}V(\vec{r}-\vec{r}')d^3r', \quad I_{v'\vec{k}',v\vec{k}} \equiv \frac{1}{\Omega_{UC}} \int u_{v'\vec{k}'}^*(\vec{r}')u_{v\vec{k}}(\vec{r}')d^3r'.\end{aligned}$$

Making a similar approximation for the r -integration, we then find

$$\begin{aligned}\langle v\vec{k} | V_C | v'c'\vec{k}' \rangle &= \frac{1}{\varepsilon\Omega^2} I_{v'\vec{k}',v\vec{k}} I_{c'\vec{k}',c\vec{k}}^* \iint e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}'-\vec{r})} V(\vec{r}-\vec{r}') d^3r d^3r' \\ &= \frac{1}{\varepsilon\Omega} I_{v'\vec{k}',v\vec{k}} I_{c'\vec{k}',c\vec{k}}^* \int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r}) d^3r.\end{aligned}$$

In a completely analogous manner, the exchange integral becomes

$$\langle v\vec{k} | V_x | v'c'\vec{k}' \rangle = \frac{1}{\Omega} I_{c\vec{k},v\vec{k}} I_{c'\vec{k}',v'\vec{k}'}^* \int V(\vec{r}) d^3r.$$

Now, at $\vec{k} = \vec{k}'$ we have $I_{\alpha\vec{k},\beta\vec{k}} = \delta_{\alpha\beta}$. Hence, if the k -dependence is not too severe we may assume that $I_{\alpha\vec{k},\beta\vec{k}'} = \delta_{\alpha\beta}$ hold approximately to a reasonable degree even when $\vec{k} \neq \vec{k}'$. In this case, we find the much simpler approximations

$$\begin{aligned}\langle v\vec{k} | V_C | v'c'\vec{k}' \rangle &\approx \frac{1}{\varepsilon\Omega} \int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r}) d^3r \delta_{vv'} \delta_{cc'} \\ \langle v\vec{k} | V_x | v'c'\vec{k}' \rangle &\approx 0.\end{aligned}$$

Hence, the bands decouple and we can focus on a single pair v and c . The Hamiltonian matrix elements become

$$H_{\vec{k},\vec{k}'} = [\tilde{E}_{c\vec{k}} - \tilde{E}_{v\vec{k}}] \delta_{\vec{k}\vec{k}'} - \frac{1}{\varepsilon\Omega} \int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r}) d^3r,$$

where we have skipped the band indices on the matrix elements. Also, the unknown expansion coefficients can be re-labeled according to $\Psi_{ij} \rightarrow \Psi_{\vec{k}}$. It follows that the exciton eigenvalue problem is now

$$[\tilde{E}_{c\vec{k}} - \tilde{E}_{v\vec{k}}] \Psi_{\vec{k}} - \frac{1}{\varepsilon\Omega} \sum_{\vec{k}'} \int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r}) d^3r \Psi_{\vec{k}'} = E_{exc} \Psi_{\vec{k}}.$$

Here, the \vec{k}' summation can be turned into an integral, i.e.

$$[\tilde{E}_{c\vec{k}} - \tilde{E}_{v\vec{k}}] \Psi_{\vec{k}} - \frac{1}{(2\pi)^3 \varepsilon} \int \int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r}) d^3r \Psi_{\vec{k}'} d^3k' = E_{exc} \Psi_{\vec{k}}.$$

The final approximation of the Wannier model consists in applying the effective mass dispersion for both bands so that

$$\tilde{E}_{c\vec{k}} \approx E_g + \frac{\hbar^2 k^2}{2m_e}, \quad \tilde{E}_{v\vec{k}} \approx -\frac{\hbar^2 k^2}{2m_h} \Rightarrow \tilde{E}_{c\vec{k}} - \tilde{E}_{v\vec{k}} \approx E_g + \frac{\hbar^2 k^2}{2m_{eh}}.$$

In this way, the k -space eigenproblem can be transformed into physical space by means of a simple inverse Fourier transform:

$$\frac{\sqrt{\Omega}}{(2\pi)^3} \int e^{i\vec{k}\cdot\vec{r}} \Psi_{\vec{k}} d^3k = \Psi_{exc}(\vec{r}), \quad \frac{\sqrt{\Omega}}{(2\pi)^3} \int e^{i\vec{k}\cdot\vec{r}} k^2 \Psi_{\vec{k}} d^3k = -\nabla^2 \Psi_{exc}(\vec{r}).$$

The $\sqrt{\Omega}$ factors are inserted to ensure that $\Psi_{exc}(\vec{r})$ is normalized. Moreover, the Coulomb term above is simply the convolution between the wave function and the Coulomb potential and, hence, we finally find

$$\left(E_g - \frac{\hbar^2 \nabla^2}{2m_{eh}} \right) \Psi_{exc}(\vec{r}) - \frac{1}{\varepsilon} V(\vec{r}) \Psi_{exc}(\vec{r}) = E_{exc} \Psi_{exc}(\vec{r}). \quad (9.4)$$

It is apparent that this so-called Wannier equation is mathematically similar to the Schrödinger equation for the hydrogen atom. The differences are that m_{eh} replaces the reduced electron-nucleus mass and that ε screens the Coulomb term. The physical interpretation is that the positive hole and negative electron interact via an attractive Coulomb potential. We note that only the relative motion of the electron-hole pair is present in the problem, so that the states have a vanishing centre-of-mass momentum. This is a consequence of our retaining only $v\vec{k} \rightarrow c\vec{k}$ excitations in the expansion, i.e. neglecting photon momentum. Hence, the centre-of-mass momentum must vanish both before and after the photon is emitted/absorbed.

To eventually calculate the optical properties, we need the momentum matrix element Eq.(9.2), which now reads as

$$\langle 0 | \hat{p}_z | exc \rangle = \sqrt{2} \sum_{\vec{k}} \Psi_{\vec{k}} \langle v\vec{k} | \hat{p}_z | c\vec{k} \rangle = \frac{\sqrt{2}\Omega}{(2\pi)^3} \int \langle v\vec{k} | \hat{p}_z | c\vec{k} \rangle \Psi_{\vec{k}} d^3k.$$

As a simplification, we make take the single-electron momentum matrix element independent of \vec{k} so that $\langle v\vec{k} | \hat{p}_z | c\vec{k} \rangle \approx p_{vc}$, which means that

$$\langle 0 | \hat{p}_z | exc \rangle \approx \frac{\sqrt{2}\Omega}{(2\pi)^3} p_{vc} \int \Psi_{\vec{k}} d^3k = \sqrt{2}\Omega p_{vc} \Psi_{exc}(0),$$

where $\Psi_{exc}(0)$ is the exciton wave function in physical space evaluated at the origin. This leads to a simple expression for the optical response

$$\chi(\omega) = \frac{4e^2\hbar^2 |p_{vc}|^2}{\varepsilon_0 m^2} \sum_{exc} \frac{|\Psi_{exc}(0)|^2}{E_{exc} [E_{exc}^2 - \hbar^2(\omega + i\Gamma)^2]} \quad (9.5)$$

In this approximation, only exciton states that are finite at the origin (“s-type”) contribute to the response. In the following, we evaluate the imaginary part in the limit of vanishing broadening

$$\text{Im } \chi(\omega) = \frac{2\pi e^2 |p_{vc}|^2}{\varepsilon_0 m^2 \omega^2} \sum_{exc} |\Psi_{exc}(0)|^2 \delta(E_{exc} - \hbar\omega) \quad (9.6)$$

for bulk and low-dimensional cases.

Exercise: Natural exciton units

The Wannier equation Eq.(9.4) is formulated in SI units and it is advantageous to switch to more natural units.

a) Show that using $a_B^* = 4\pi\varepsilon\varepsilon_0\hbar^2 / m_{eh}e^2$ as the unit of length and $Ry^* = \hbar^2 / 2m_{eh}a_B^{*2}$ as the energy unit, the Wannier equation reduces to

$$(E_g - \nabla^2)\Psi_{exc}(\vec{r}) - \frac{2}{r}\Psi_{exc}(\vec{r}) = E_{exc}\Psi_{exc}(\vec{r}).$$

b) Show that $a_B^* = 0.529\text{\AA} \cdot \varepsilon m / m_{eh}$ and $Ry^* = 13.6\text{eV} \cdot m_{eh} / \varepsilon^2 m$ (m is the free electron mass) and evaluate both for GaAs: $m_e = 0.066 m$, $m_h = 0.5 m$ (heavy hole), $\varepsilon = 12.9$ and for ZnO: $m_e = 0.28 m$, $m_h = 0.59 m$ (heavy hole), $\varepsilon = 6.7$ (incl. eff. phonon contribution).

References

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