

10. Excitons in Bulk and Two-dimensional Semiconductors

The Wannier model derived in the previous chapter provides a simple framework for the inclusion of excitons in the optical properties of semiconductors. In this chapter, we will evaluate the optical response for 3D and 2D semiconductors. As will become apparent, excitonic effects in low-dimensional semiconductors are hugely enhanced. The reason is that excitonic effects originate from the attractive interaction between electrons and holes. The stronger the attraction, the more pronounced the excitonic corrections to the response. But an additional confinement will also tend to localize electrons and holes in the same region of space and, hence, increase the overlap of their wave functions. This may increase the Coulomb attraction significantly.

We begin by investigating the 3D or bulk case. The starting point is the Wannier equation written in natural exciton units (using a_B^* and Ry^* as the units of length and energy, respectively)

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

The expression for the susceptibility Eq.(9.5) shows that only s-type eigenstates are relevant. These are nothing but the usual eigenstates of the hydrogen atom. For the bound states with energy below E_g we have in terms of the principle quantum number $n = 1, 2, 3, \dots$,

$$\Psi_n(\vec{r}) = \frac{1}{\sqrt{\pi}n^{5/2}}L_{n-1}^1(2r/n)e^{-r/n}, \quad E_n = E_g - \frac{1}{n^2}.$$

Here, L_n^m is an associated Laguerre polynomial. As we use Ry^* as the unit of energy it follows that these states form a series of resonances located spectrally between E_g and $E_g - Ry^*$. Hence, bound excitons lead to discrete absorption peaks below the band gap. The continuum states with $E > E_g$ are harder, in part because they cannot be normalized in the usual sense. To circumvent this problem, we enclose the exciton in a large sphere of radius R [1]. We let the wave function vanish on the surface of the sphere and eventually let the radius go to infinity. We write $\alpha^2 = E - E_g$ so that the radial Schrödinger equation becomes

$$-\frac{1}{r}\frac{d^2}{dr^2}r\Psi(r) - \frac{2}{r}\Psi(r) = \alpha^2\Psi(r).$$

A solution is

$$\Psi_\alpha(r) = Ne^{-i\alpha r} F(1 + i/\alpha, 2; 2i\alpha r),$$

where F is called a confluent hypergeometric function (see e.g. [2] for details). We need to study the behavior as r approaches R to fulfill the boundary conditions. Since R is eventually taken very large, we can use the asymptotic expression for F . We can also apply the asymptotic expression to determine the normalization constant N because we mainly integrate over a region with r large. The asymptotic limit is

$$\begin{aligned} |F(1 + i/\alpha, 2; 2i\alpha r)|^2 &\approx \left| -\frac{2(2i\alpha r)^{1+i/\alpha}}{\Gamma(1-i/\alpha)} + \frac{2(-2i\alpha r)^{1-i/\alpha}}{\Gamma(1+i/\alpha)} \right|^2 \\ &= \frac{e^{-\pi/\alpha} \sinh(\pi/\alpha)}{\pi\alpha r^2} \cos^2(\alpha r). \end{aligned}$$

Hence, to normalize we integrate within the sphere

$$1 = 4\pi \int_0^R |\Psi_\alpha(r)|^2 r^2 dr = N^2 \frac{2 \sinh(\pi/\alpha)}{\alpha e^{\pi/\alpha}} R.$$

It follows that the wave function at the origin is given by

$$|\Psi(0)|^2 = \begin{cases} \frac{1}{\pi n^3}, & E = E_g - \frac{1}{n^2} \quad \text{bound states } E < E_g \\ \frac{\alpha e^{\pi/\alpha}}{2R \sinh(\pi/\alpha)}, & E = E_g + \alpha^2 \quad \text{continuum } E > E_g. \end{cases}$$

The main remaining problem lies in summing the continuum solutions while taking $R \rightarrow \infty$. For this purpose we introduce the weighted joint density of states

$$S(\omega) = \sum_{\text{cont.}} |\Psi(0)|^2 \delta(E - \hbar\omega),$$

where the sum is over all continuum states. From the asymptotic expression for the wave function above, it is clear that the allowed values of α fulfill $\alpha R = \pi(p + 1/2)$, where p is an integer. Hence, the distance between allowed values of α is $\delta\alpha = \pi/R$. We can therefore write the sum as

$$S(\omega) = \sum_\alpha \frac{\alpha e^{\pi/\alpha}}{2\pi \sinh(\pi/\alpha)} \delta(E_g + \alpha^2 - \hbar\omega) \delta\alpha.$$

Taking $R \rightarrow \infty$ means $\delta\alpha \rightarrow 0$ and so, converting to an integral, we find the simple result

$$\begin{aligned}
S(\omega) &= \int_0^\infty \frac{\alpha e^{\pi/\alpha}}{2\pi \sinh(\pi/\alpha)} \delta(E_g + \alpha^2 - \hbar\omega) d\alpha \\
&= \frac{\theta(\hbar\omega - E_g) e^{\pi/\sqrt{\hbar\omega - E_g}}}{4\pi \sinh(\pi/\sqrt{\hbar\omega - E_g})},
\end{aligned} \tag{10.1}$$

where θ is the unit step function. Reverting to SI units means reintroducing a_B^* and Ry^* . Since S has units of $\text{length}^{-3} \cdot \text{energy}^{-1}$ we need to divide by a factor $a_B^{*3} Ry^* = \hbar^3 / (2m_{eh})^{3/2} / \sqrt{Ry^*}$ using the relation $a_B^{*2} Ry^* = \hbar^2 / 2m_{eh}$ and we can then write the final result as

$$\text{Im } \chi(\omega) = \frac{e^2 |p_{vc}|^2 \sqrt{Ry^*}}{2\varepsilon_0 m^2 \omega^2} \left(\frac{2m_{eh}}{\hbar^2} \right)^{3/2} \left\{ \sum_n \frac{4}{n^3} \delta(\Delta + 1/n^2) + \frac{\theta(\Delta) e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})} \right\},$$

with $\Delta = (\hbar\omega - E_g) / Ry^*$. This formula is called the 3D Elliott formula. Based on this result, the real part can be obtained using the Kramers-Kronig relations and broadening can be introduced through convolution with a Lorentzian broadening function. This leads to the expression

$$\chi(\omega) = \frac{e^2 \hbar^2 |p_{vc}|^2}{\pi^2 \varepsilon_0 m^2 E_g^{3/2}} \left(\frac{2m_{eh}}{\hbar^2} \right)^{3/2} X_3(w),$$

where $X_3(w)$ is now the excitonic susceptibility function given by [3]

$$\begin{aligned}
X_3(w) &= \frac{\pi Ry^{*1/2} E_g^{3/2}}{2(\hbar w)^2} \left\{ \sum_n \frac{8Ry^* (\hbar w)^2}{n^3 E_n [E_n^2 - (\hbar w)^2]} + g \left(\sqrt{\frac{Ry^*}{E_g - \hbar w}} \right) + g \left(\sqrt{\frac{Ry^*}{E_g + \hbar w}} \right) - 2g \left(\sqrt{\frac{Ry^*}{E_g}} \right) \right\} \\
g(z) &\equiv 2 \ln(z) + 2\psi(z) + \frac{1}{z}, \quad \psi(z): \text{ digamma function,}
\end{aligned}$$

where $w = \omega + i\Gamma$ and $E_n = E_g - \frac{Ry^*}{n^2}$ is the energy of the n 'th bound exciton. In Fig. 10.1, the real and imaginary parts are plotted for a 3D material with $E_g = 1.5$ eV and varying values of the effective Rydberg and broadening.

To see that the Elliott formula has the correct limiting behavior if Coulomb effects become negligible (if e.g. ε becomes very large) we should take $Ry^* \rightarrow 0$ and accordingly $\Delta \rightarrow \infty$. We note that

$$\lim_{\Delta \rightarrow \infty} \frac{e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})} = \frac{\sqrt{\Delta}}{\pi}.$$

Also, the contribution from bound excitons vanishes. Hence, we find the approximate expression

$$\text{Im } \chi(\omega) = \frac{e^2 |p_{vc}|^2}{2\pi\epsilon_0 m^2 \omega^2} \left(\frac{2m_{eh}}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g} \theta(\hbar\omega - E_g).$$

This expression is identical to the imaginary part of the independent-electron result Eq.(8.2) if vanishing broadening is assumed.

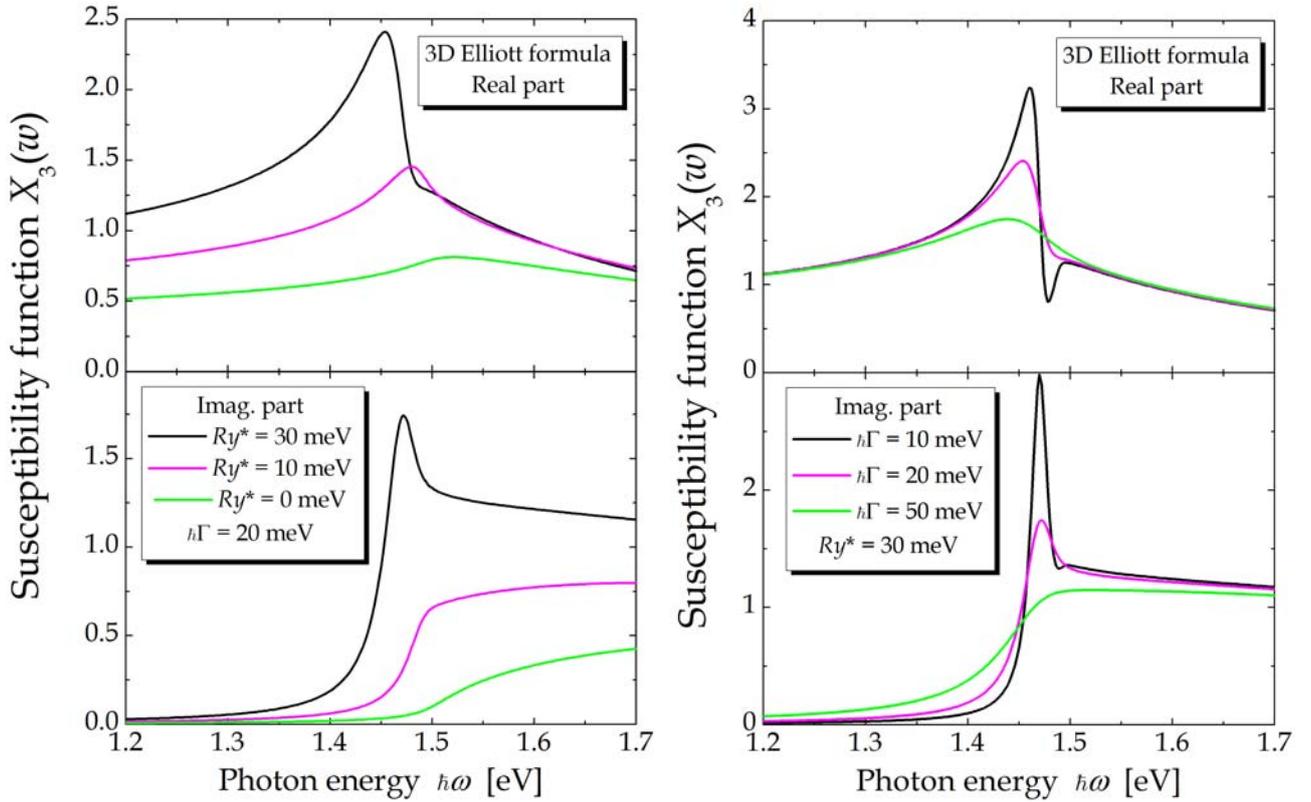


Figure 10.1 The excitonic susceptibility function for a bulk semiconductor. The plots illustrate the effect of varying the strength of the Coulomb interaction (left panels) and broadening (right panels).

10.1 Excitons in Quantum Wells

We will consider the case of an electron-hole pair confined to a thin quantum well. It is assumed that light is polarized along the quantum well plane so that the motion perpendicular to the plane (taken as the z direction) is not excited. As in the 3D case, we therefore require a vanishing centre-of-mass momentum in the plane. Hence, for the in-plane motion only the relative part is retained and the electron-hole pair is characterized by a Hamiltonian (in polar coordinates)

$$\hat{H}_{eh} = \hat{h}_e(z_e) + \hat{h}_h(z_h) + E_g - \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r^2} \frac{d^2}{d\theta^2} - \frac{2}{\sqrt{r^2 + (z_e - z_h)^2}}. \quad (10.2)$$

Here, $\hat{h}_e(z_e) = -m_e^{-1} d^2 / dz_e^2 + V_e(z_e)$ is the Hamiltonian for the z motion of the electron confined by the quantum well potential V_e and $\hat{h}_h(z_h)$ is the analogous term for the hole. We will now specialize to the idealized case of an exciton confined to an extremely thin quantum well. The strong confinement means that $z_e \approx z_h$ and so we will use the simplifying approximation

$$\frac{2}{\sqrt{r^2 + (z_e - z_h)^2}} \approx \frac{2}{r}. \quad (10.3)$$

This means that the Hamiltonian becomes a sum $\hat{H}_{eh} = \hat{h}_e(z_e) + \hat{h}_h(z_h) + \hat{H}(r)$, where $\hat{H}(r)$ describes the in-plane relative motion. As a consequence, the exciton wave function is a product $\Psi_{exc}(\vec{r}_e, \vec{r}_h) = \varphi_e(z_e) \varphi_h(z_h) \Psi(\vec{r})$, where φ_e is an eigenstate of \hat{h}_e and similarly for the hole. We assume that the z -motion of both electrons and holes are frozen in the lowest eigenstates. This amounts to replacing the true band gap E_g by the effective one $\tilde{E}_g = E_g + E_1^e + E_1^h$, where $E_1^e + E_1^h$ is the sum of electron and hole quantization energies (in previous chapter we used the notation E_{g11} for \tilde{E}_g). The in-plane relative motion then leads to a purely two-dimensional Wannier equation given in polar coordinates by

$$\left(\tilde{E}_g - \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r^2} \frac{d^2}{d\theta^2} \right) \Psi(\vec{r}) - \frac{2}{r} \Psi(\vec{r}) = E \Psi(\vec{r}).$$

This problem is mathematically identical to a hydrogen atom in two dimensions. The s -type bound states (with no angular dependence) are quite similar to the 3D case and can be written

$$\Psi_n(\vec{r}) = \frac{1}{\sqrt{\pi} (n + \frac{1}{2})^{3/2}} L_n(2r / (n + \frac{1}{2})) e^{-r / (n + \frac{1}{2})}, \quad E_n = \tilde{E}_g - \frac{1}{(n + \frac{1}{2})^2}.$$

Here, the principle quantum number n is again an integer, but now the allowed values include zero, i.e. $n = 0, 1, 2, \dots$. The most important feature of this result compared to the 3D case is that the binding energy of the lowest exciton is now $4Ry^*$ whereas excitons in bulk were bound by no more than $1Ry^*$. This is a direct manifestation of the increased electron-hole overlap in low-dimensional geometries. The continuum states are also highly similar to the bulk case and found to be

$$\Psi_\alpha(r) = N e^{-i\alpha r} F\left(\frac{1}{2} + i/\alpha, 1; 2i\alpha r\right),$$

with a normalization condition that is now

$$1 = 2\pi \int_0^R |\Psi_\alpha(r)|^2 r dr = N^2 \frac{2 \cosh(\pi/\alpha)}{\alpha e^{\pi/\alpha}} R.$$

This result corresponds to normalization within a circle of radius R . Eventually, it follows that the wave function at the origin is given by

$$|\Psi(0)|^2 = \begin{cases} \frac{1}{\pi(n + \frac{1}{2})^3}, & E = \tilde{E}_g - \frac{1}{(n + \frac{1}{2})^2} \text{ bound states } E < \tilde{E}_g \\ \frac{\alpha e^{\pi/\alpha}}{2R \cosh(\pi/\alpha)}, & E = \tilde{E}_g + \alpha^2 \text{ continuum } E > \tilde{E}_g. \end{cases}$$

Summing over the continuum states leads to a result identical to Eq.(10.1) except that sinh is replaced by cosh. Finally, we arrive at a 2D Elliott formula describing the excitonic absorption in an ultrathin quantum well of width d :

$$\text{Im } \chi(\omega) = \frac{e^2 |p_{vc}|^2 m_{eh}}{\varepsilon_0 m^2 \hbar^2 \omega^2 d} \left\{ \sum_n \frac{4}{(n + \frac{1}{2})^3} \delta(\Delta + 1/(n + \frac{1}{2})^2) + \frac{\theta(\Delta) e^{\pi/\sqrt{\Delta}}}{\cosh(\pi/\sqrt{\Delta})} \right\}.$$

Here, $\Delta = (\hbar\omega - \tilde{E}_g)/Ry^*$ and the relation $a_B^* Ry^* = \hbar^2 / 2m_{eh}$ has been utilized. Also, it is clear that in the limit of independent electrons we find

$$\text{Im } \chi(\omega) = \frac{e^2 |p_{vc}|^2 m_{eh}}{\varepsilon_0 m^2 \hbar^2 \omega^2 d} \theta(\hbar\omega - \tilde{E}_g),$$

in agreement with chapter 8. Again, broadening can be introduced and the real part can be added so that the full 2D excitonic susceptibility becomes

$$\chi(\omega) = \frac{2e^2 |p_{vc}|^2 m_{eh}}{\pi \varepsilon_0 m^2 \tilde{E}_g^2 d} X_2(\omega),$$

with the susceptibility function [4]

$$X_2(\omega) = \frac{2\tilde{E}_g^2}{(\hbar\omega)^2} \left\{ \sum_n \frac{8Ry^* (\hbar\omega)^2}{(n + \frac{1}{2})^3 E_n [E_n^2 - (\hbar\omega)^2]} + f \left(\sqrt{\frac{Ry^*}{\tilde{E}_g - \hbar\omega}} \right) + f \left(\sqrt{\frac{Ry^*}{\tilde{E}_g + \hbar\omega}} \right) - 2f \left(\sqrt{\frac{Ry^*}{\tilde{E}_g}} \right) \right\}$$

$$f(z) \equiv 2 \ln(z) + 2\psi(z + \frac{1}{2}), \quad \psi(z): \text{ digamma function,}$$

where $w = \omega + i\Gamma$ and $E_n = \tilde{E}_g - \frac{Ry^*}{(n + \frac{1}{2})^2}$ is the energy of the n 'th bound exciton. In Fig. 10.2, we have plotted this result. It is clearly seen that excitons lead to a complete reorganization of the spectra. A huge excitonic resonance located $4Ry^*$ below the band gap emerges but also the continuum part of the spectrum is severely modified.

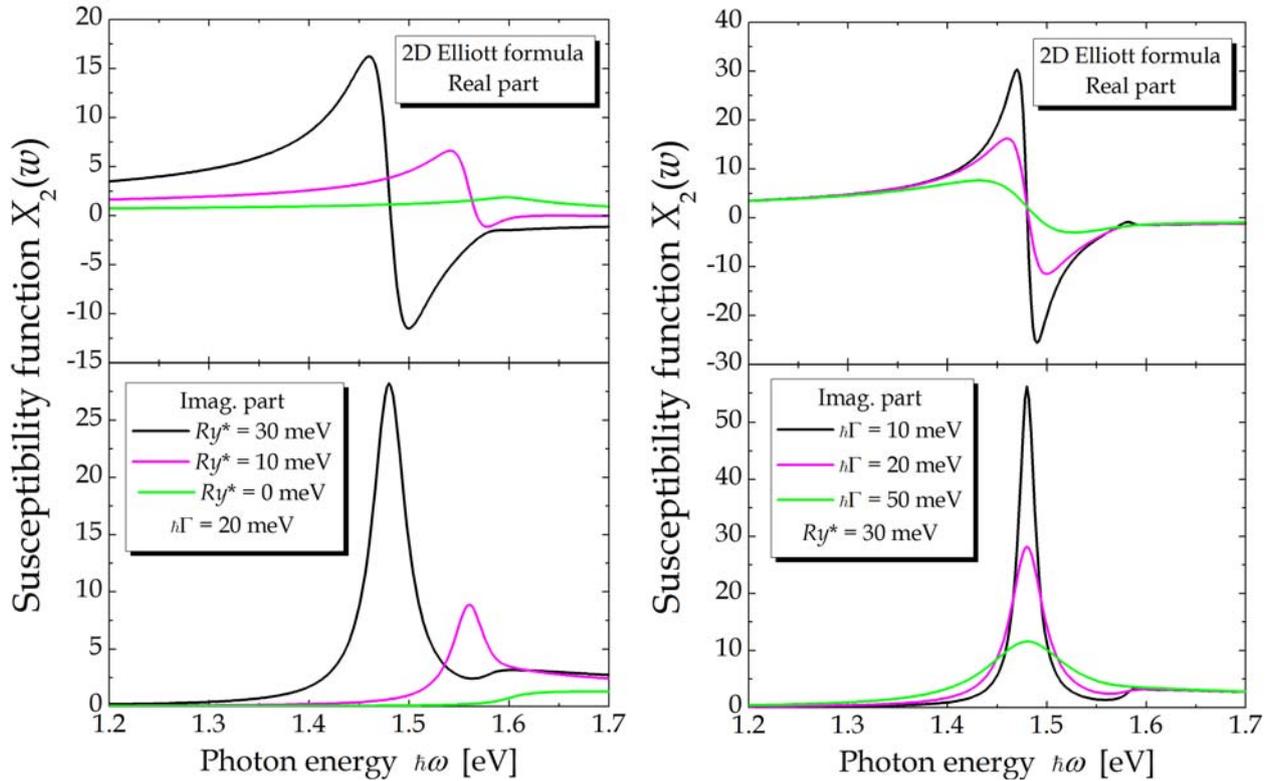


Figure 10.2 The excitonic susceptibility function for a semiconductor quantum well. In the plots, the effective band gap is taken as 1.6 eV.

Exercise: Variational treatment of quantum well excitons

In this exercise, we will return to the quantum well Hamiltonian Eq.(10.2) and look for more accurate solutions. Primarily, we will not apply the simple approximation Eq.(10.3). However, we will still look for solutions of the form $\Psi_{exc}(\vec{r}_e, \vec{r}_h) = \varphi_e(z_e)\varphi_h(z_h)\Psi(\vec{r})$ with φ_e an eigenstate of \hat{h}_e and similarly for the hole. Hence, the improvement lies in finding a better estimate for $\Psi(\vec{r})$ and for this purpose we will use the variational method.

a) Show using Eq.(10.2) that the expectation value for the energy is

$$E = \tilde{E}_g + \langle \Psi(\vec{r}) | -\frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r^2} \frac{d^2}{d\theta^2} + V(r) | \Psi(\vec{r}) \rangle,$$

with an effective potential

$$V(r) = -2 \iint \frac{|\varphi_e(z_e)\varphi_h(z_h)|^2}{\sqrt{r^2 + (z_e - z_h)^2}} dz_e dz_h,$$

As a simple example, we consider a quantum well of width d with infinite barriers. This means that the eigenstates for the z -motion are $\varphi(z) = \sqrt{\frac{2}{d}} \sin(\frac{\pi z}{d})$.

b) Using $u = (z_e - z_h)/d$ and $v = (z_e + z_h)/d$ show that

$$V(r) = -\frac{8}{d} \int_0^1 \int_u^{2-u} \frac{\sin^2(\frac{u+v}{2}) \sin^2(\frac{u-v}{2})}{\sqrt{(r/d)^2 + u^2}} dv du.$$

Evaluating the v integral, we find

$$V(r) = -\frac{2}{d} \int_0^1 \frac{h(u)}{\sqrt{(r/d)^2 + u^2}} du.$$

with $h(u) = (1-u)[2 + \cos(2\pi u)] + \frac{3}{2\pi} \sin(2\pi u)$. As a particular variational ansatz, we will try the form $\Psi(\vec{r}) = \sqrt{\frac{2}{\pi}} \alpha e^{-\alpha r}$.

c) Show that the ansatz is normalized and that the kinetic energy is α^2 . Use these results to demonstrate that

$$E = \tilde{E}_g + \alpha^2 + \int_0^1 h(u) W(u) du,$$

where $W(u) = -\frac{8\alpha^2}{d} \int_0^\infty \frac{e^{-2\alpha r} r}{\sqrt{(r/d)^2 + u^2}} dr.$

It can be shown that $W(u) = 4\pi u \alpha^2 d \{ \frac{2}{\pi} + Y_1(2u\alpha d) - H_1(2u\alpha d) \}$, where Y_1 and H_1 are Bessel and Struve functions, respectively. If d is sufficiently small, this rather complicated expression may be approximated by the 1. order expansion $W(u) \approx -4\alpha + 8u\alpha^2 d$.

d) Show that

$$E \approx \tilde{E}_g + \alpha^2 - 4\alpha + \left(\frac{8}{3} - \frac{10}{\pi^2} \right) \alpha^2 d,$$

and that by minimizing with respect to α that the optimal energy E_0 is given by

$$E_0 \approx \tilde{E}_g - \frac{4}{1 + \left(\frac{8}{3} - \frac{10}{\pi^2}\right)d}.$$

In the plot below, the exciton binding energy is plotted versus the width of the quantum well, both in natural exciton units.

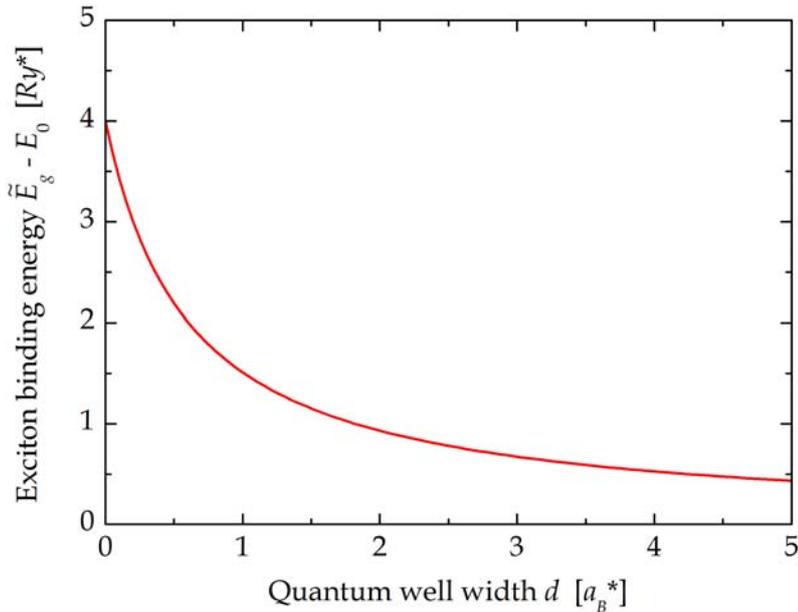


Figure 10.3 Variational calculation of the binding energy of excitons in a semiconductor quantum well.

References

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