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Variational methods for calculating exciton binding energies in quantum well structures

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Abstract. A new and powerful mathematical technique is described for evaluating the binding energies of excitons within the framework of the variational method. The technique is applied to infinite wells and the binding energies of 1s- and 2s-type excitons calculated as a function of well width.

1. Introduction

It is well known that the characteristic emission from multiple quantum well structures occurs via exciton emission (Chang *et al* 1988). In a real solid there are many complicating effects which preclude a simple comparison of the experimental observation of the exciton emission energy with the theoretical estimate of this value. This arises from uncertainty in the knowledge of a whole range of parameters included among which are the value of the band offsets, the magnitude of the internal strain, the exact widths of the wells and barriers, the relevant effective mass parameters and the degenerate nature of the valence band states. It is therefore essential to have some method which enables a reliable estimate to be made of the binding energy of the exciton once the values of the above parameters are known. In this regard we note that it is standard in the literature (Miller *et al* 1982, Greene and Bajaj 1983, Wu and Nurmikko 1987, Chang *et al* 1988) to employ trial wavefunctions for the relative motion of the electron and hole and invoke the variational principle as a criterion for obtaining the 'best' estimate of the binding energy of the exciton. The purpose of the present paper is to describe a new and powerful mathematical method which enables accurate evaluation of the binding energy of the exciton given a particular choice of variational wavefunction. The approach should permit easier and more accurate evaluation of exciton binding energies than hitherto.

In order to illustrate the method we consider the situation where the electron and hole are confined in the same region of space in an infinitely deep potential well. This serves the dual purpose of keeping the formalism relatively simple, thus enabling the essential mathematical steps involved to be clearly displayed, while providing a check on the validity of the theory in the limit of a quantum well of zero width, as described in greater detail below.

2. Method

The quantum well structure appropriate to the present problem corresponds to a single rectangular quantum well of width L in the z -direction, but of infinite extent in the

xy plane. The energy levels of an exciton in such a structure can be described in terms of the effective mass approximation (Chang *et al* 1988, Wu and Nurmikko 1988, Wu 1988). The appropriate Hamiltonian H_{eff} consists of two single particle Hamiltonians $h_e(z_e)$ and $h_h(z_h)$ describing the separate motions of the electron and hole respectively, together with an interaction term h_{rel} representing their relative motion and arising from the Coulombic interaction term. Thus

$$H_{\text{eff}} = h_e(z_e) + h_h(z_h) + h_{\text{rel}} \quad (1)$$

where, for example,

$$h_e(z_e) = \frac{p_{ze}^2}{2m_e} + \theta(|z_e| - \frac{1}{2}L) V_\infty \quad (2)$$

and $\theta(\tau)$ is the Heaviside unit step function. An analogous expression holds for $h_h(z_h)$. Similarly

$$h_{\text{rel}} = \frac{p_\perp^2}{2\mu} - \frac{e^2}{\epsilon[r_\perp^2 + (z_e - z_h)^2]^{1/2}} \quad (3)$$

where the relative motion in the xy plane is assigned a coordinate r_\perp , a momentum p_\perp an effective (reduced) mass μ and the medium is taken to have a dielectric constant ϵ .

The solution to the exciton Hamiltonian H_{eff} is obtained via a variational approach employing a trial wavefunction of the form (Chang *et al* 1988, Greene and Bajaj 1983, Wu and Nurmikko 1987, Bastard *et al* 1974, Wu and Nurmikko 1988, Wu 1988)

$$\Psi(r_\perp, z_e, z_h) = \Psi_e(z_e)\Psi_h(z_h)\varphi_{e-h}(r_\perp, |z_e - z_h|) \quad (4)$$

where Ψ_e (Ψ_h) are the electron (hole) one-particle eigenfunctions of the Hamiltonian $h_e(z_e)$ [$h_h(z_h)$] having eigenvalues E_e (E_h) and $\varphi_{e-h}(r_\perp, |z_e - z_h|)$ is the wavefunction describing the relative motion of the electron and hole.

Within such an approach we are led to the problem of evaluating an energy term, E_b , where

$$E_b = \frac{\int \Psi(r_\perp, z_e, z_h)^* h_{\text{rel}} \Psi(r_\perp, z_e, z_h) dz_e dz_h d^2 r_\perp}{\int \Psi(r_\perp, z_e, z_h)^* \Psi(r_\perp, z_e, z_h) dz_e dz_h d^2 r_\perp} \quad (5)$$

and is a measure of the binding energy of the exciton.

The present paper is not concerned with the validity or otherwise of the so-called envelope function approximation which results in the above formalism, but deals solely with effecting great simplifications in evaluating the expression for E_b appearing in (5). In order to illustrate the essential features of the present approach, and to contrast it with the standard technique employed to solve for E_b , we consider first evaluating the electron-hole correlation energy. It follows from (5) that the latter has the form

$$-\frac{e^2}{N\epsilon} \int \frac{|\Psi_e(z_e)|^2 |\Psi_h(z_h)|^2 |\varphi_{e-h}(r_\perp, |z_e - z_h|)|^2}{(r_\perp^2 + |z_e - z_h|^2)^{1/2}} dz_e dz_h d^2 r_\perp \quad (6)$$

where the normalization integral

$$N = \int \Psi^*(r_\perp, z_e, z_h) \Psi(r_\perp, z_e, z_h) dz_e dz_h d^2 r_\perp. \quad (7)$$

Carrying out the integration over the xy plane will lead to a term

$$I = \int \frac{|\varphi_{e-h}(r_\perp, |z_e - z_h|)|^2}{(r_\perp^2 + |z_e - z_h|^2)^{1/2}} d^2 r_\perp. \quad (8)$$

Because of the presumed functional form of φ_{e-h} , the ensuing value of I will be a function of $a = |z_e - z_h|$ only, i.e.

$$I = I(a).$$

Employing this notation we can then rewrite (6) in the form

$$-\frac{e^2}{N\epsilon} \int |\Psi_e(z_e)|^2 |\Psi_h(z_h)|^2 I(a) dz_e dz_h$$

which, with a simple change of variable, can be rewritten in the form

$$-\frac{e^2}{N\epsilon} \int p(a) I(a) da \quad (9)$$

for an appropriately defined value of $p(a)$.

The utility of such an approach is that it avoids expanding the denominator of (6) in terms of a complete set of functions (typically modified Bessel functions) as is normally done (Chan *et al* 1988, Wu and Nurmikko 1987, 1988, Wu 1988). In further illustration of the method, consider the specific problem at hand, namely an infinitely deep potential well of width L . For this situation the (normalized) wavefunctions are given by

$$\Psi = \Psi_e = \Psi_h = \left(\frac{2}{L}\right)^{1/2} \sin \frac{\pi z}{L}. \quad (10)$$

For the situation where $a \neq 0$ we readily obtain, by expeditious use of the two Dirac delta functions $\delta(z_e - z_h - a)$ and $\delta(z_h - z_e - a)$ that

$$\begin{aligned} p(a) &= \int |\Psi_e(z_e)|^2 |\Psi_h(z_h)|^2 [\delta(z_e - z_h - a) + \delta(z_h - z_e - a)] dz_e dz_h \\ &= 2 \int_0^{L-a} |\Psi(x)|^2 |\Psi(x+a)|^2 dx \\ &= \frac{2}{L^2} \left[\left(\frac{L-a}{2}\right) \left(\cos \frac{2\pi a}{2} + 2\right) + \frac{3L}{4\pi} \sin \frac{2\pi a}{L} \right]. \end{aligned} \quad (11)$$

(It is interesting to note that $p(a) da$ is a measure of the (uncorrelated) probability of finding an electron and hole, the magnitude of whose separation along the z -axis lies between a and $a + da$).

The next step is concerned with the evaluation of the integral $I(a)$. To illustrate the method we consider two examples. In the first example we will employ, for the relative motion of the electron and hole, a trial wavefunction that has been used extensively in the literature (Chang *et al* 1988, Wu and Nurmikko 1987, 1988, Wu 1988), and which contains no dependence on $|z_e - z_h|$, namely

$$\varphi_{e-h}(r_{\perp}, a) = \varphi_{e-h}(r_{\perp}) = \left(\frac{2}{\pi}\right)^{1/2} \lambda^{-1} \exp\left(-\frac{r_{\perp}}{\lambda}\right) \quad (12)$$

where $r_{\perp}^2 = x^2 + y^2$.

Note, with this choice of trial function, the kinetic energy term in h_{rel} can be trivially evaluated and has the form $\hbar^2/2\mu\lambda^2$. Substituting (12) into (9) gives, apart from a factor of $4/\lambda^2$,

$$I(a) = \int_0^{\infty} \frac{e^{-ar_{\perp}} r_{\perp} dr_{\perp}}{[r_{\perp}^2 + a^2]^{1/2}} \quad (13)$$

where $\alpha = 2/\lambda$. It is expedient for later manipulations to consider the special case of this integral corresponding to $a = 0$, i.e.

$$I(0) = \int_0^\infty e^{-\alpha r_\perp} dr_\perp = \frac{1}{\alpha} = \frac{a}{\lambda_1} \quad (14)$$

where $\lambda_1 = a\alpha$. If in equations (13) and (14) we make the scale change

$$r_\perp = ar_\perp \quad (15)$$

followed by

$$r_\perp = \sinh \theta \quad (16)$$

we readily obtain

$$I(a) - I(0) = -a \int_0^\infty e^{-\lambda_1 \sinh \theta} [\cosh \theta - \sinh \theta] d\theta. \quad (17)$$

If we then introduce the change of variable

$$x = \cosh \theta - \sinh \theta = e^{-\theta} \quad (18)$$

we get

$$I(a) = \frac{a}{\lambda_1} - a \int_0^1 \exp\left[-\frac{\lambda_1}{2}\left(\frac{1}{x} - x\right)\right] dx \quad (19)$$

which can be readily evaluated numerically for all values of a . It is to be emphasized that this same procedure simplifies all the integrals that occur in the theory for all choices of wavefunction φ_{e-h} employed later for the electron-hole relative motion.

In order to illustrate this last point, we choose as our second example a wavefunction φ_{e-h} which possesses a dependence on $a = |z_e - z_h|$, thus we take

$$\varphi_{e-h}(r_\perp, a) \sim e^{-r/\lambda} \quad (20)$$

where $r^2 = r_\perp^2 + a^2$. For this situation the integral $I(a)$ can be trivially evaluated since

$$I(a) \sim \int_a^\infty \frac{2\pi e^{-2r/\lambda}}{r} r_\perp dr_\perp$$

but $r^2 = r_\perp^2 + a^2$ giving $r dr = r_\perp dr_\perp$ and

$$I(a) \sim \int_a^\infty e^{-2r/\lambda} dr = \frac{\lambda}{2} e^{-2a/\lambda}. \quad (21)$$

However, the evaluation of the kinetic energy terms associated with the 2D-motion in the xy plane now becomes non-trivial. In particular we have

$$\begin{aligned} & \int \varphi_{e-h} \left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \right] \varphi_{e-h} dx dy \\ & \sim -\frac{\hbar^2}{2\mu} \int_0^\infty e^{-2r/\lambda} \left(-\frac{1}{r\lambda} + \frac{1}{\lambda^2} - \frac{a^2}{\lambda r^3} - \frac{a^2}{r^2 \lambda^2} \right) 2\pi r_\perp dr_\perp. \end{aligned} \quad (22)$$

The first two integrals may be simplified in the same manner as that leading to (21). However for the last two terms we must adopt the procedure described in equations

(15), (16) and (18). In this way we can write the RHS of (22) in the form

$$-\frac{\hbar^2}{2\mu} \left\{ \frac{\pi}{2} \left(\frac{2a}{\lambda} - 1 \right) e^{-2a/\lambda} - 2\pi \int_0^1 \exp \left[-\frac{a}{\lambda} \left(x + \frac{1}{x} \right) \right] \times \left[\frac{2a}{\lambda(1+x^2)} + \frac{a^2}{x\lambda^2} \right] \left(\frac{1-x^2}{1+x^2} \right) dx \right\}$$

which can again be readily evaluated numerically for all values of a .

In summary the present technique enables us to evaluate readily all the integrals that occur in the theory for any choice of trial function of the type given in (4) without the need for recourse to a series expansion as is usually done. It also has the distinct advantage that whatever the values of a , the range of integration lies in the domain 0 to 1, and this has distinct computational advantages both for speed and, more importantly, for accuracy. We will describe next the results of the analysis for various choices of wavefunction φ_{e-h} and for differing well widths. This then enables the calculation of the binding energy of a 2s-exciton to be reliably estimated.

3. Binding energy of 1s-state and 2s-state excitons

We employed four different choices of trial wavefunction for the relative motion of the electron and hole for a 1s-state exciton. These were as follows:

$$\varphi_1 \sim e^{-r/\lambda} \quad \varphi_2 \sim e^{-r/\lambda} e^{-a/\lambda} \quad \varphi_3 \sim e^{-r/\lambda} \quad \varphi_4 \sim (1 + Ba^2) e^{-r/\lambda}$$

where, as before, $a = |z_e - z_h|$ and $r = (r_{\perp}^2 + a^2)^{1/2}$.

Using the procedure described in the previous section, the values of the parameters λ and B were then varied to give the largest numerical value for the binding energy E_b . Since in the authors' laboratory we are interested in ultimately applying the results of this analysis to the II-VI compound CdTe, we employed effective masses and a dielectric constant appropriate to this compound, together with a corresponding free exciton binding energy of 10 meV. The results of the calculation are tabulated in table 1, from which it can be seen that the function φ_1 , which is extensively employed in the literature, is not the best choice of wavefunction in the variational sense, and can lead to significant underestimates of the electron-hole correlation energy for the wider wells. However, this apart, the wavefunctions φ_2 , φ_3 and φ_4 which all contain a z dependence, give closely similar values for the exciton binding energy. This in itself is most encouraging in that it would indicate that the values of the exciton binding energy are in fact close to these theoretical values, and can in this sense be reliably estimated via such an approach. With regard to the wavefunctions themselves we note that φ_2 is an unusual function in that although it is continuous at the origin, it possess a discontinuity in its derivative there. Similarly the function φ_4 , and functions like it having the form $(1 + Ba^2 + Ca^4 + Da^2 + \dots) e^{-r/\lambda}$, offer no distinct advantage as far as evaluating the energy is concerned, despite their increased complexity. The results of the present calculations thus suggest that for real physical systems where the potential wells are of finite size, the function $e^{-r/\lambda}$ offers reliable estimates of the energy and possesses a simple, compact form which commends its use.

Having reached this conclusion we turn next to the question of reliably estimating the energy of the excited 2s-state of the exciton. If we adopt the choice for the relative motion that

$$\varphi_5 \sim \left(1 - \alpha_2 \frac{r}{\lambda_2} \right) e^{-r/\lambda_2}$$

and insist that the total wavefunction $\Psi(r_{\perp}, z_c, z_h)$ given in (4) and involving φ_5 be orthogonal to the corresponding wavefunction involving φ_3 (as demanded by quantum mechanics) we can then express α_2 in terms of the parameter λ_2 and the (already determined) parameter λ of the 1s state. The energy of the 2s state can then be readily evaluated in the manner previously described and the parameter λ_2 varied to maximize the binding energy. The results obtained in this way for various well widths, are shown in table 1. There are two interesting points that are apparent from table 1. The first concerns the magnitude of the binding energies for a vanishing well width, when the exciton becomes truly two-dimensional. For this situation the binding energy of the 1s exciton should be four times the free exciton binding energy (thus giving a value of 40 meV in agreement with the calculations). However, and more importantly, the binding energy of the 2s exciton in this limit should be 4/9 that of the free exciton, i.e. 4.44 meV. The fact that the theoretical values approach this value is gratifying, and gives confidence in the orthogonality criterion adopted above and shows that this criterion prevents 'collapse to the core' (which could occur from unrestricted variation of α_2 and λ_2) and in itself is reminiscent of similar results obtained in pseudopotential theory, which is also based on this same orthogonality criterion. The second important result is that the 2s exciton binding energy does not vary significantly for large variations in the well width. An extrapolation of this result to finite potential wells could be used to provide accurate estimates there of the 1s binding energy from observations of the energy separation of the 1s and 2s states.

Table 1. Theoretical values of binding energies from the trial functions φ_1 - φ_5 as a function of well width, L , with the corresponding values of the Bohr orbits in Å given in parenthesis. ($m_e^0 = 0.096m_e$, $m_h^0 = 0.4m_e$, $\epsilon = 9.6$).

$L(\text{Å})$	Binding energies (meV)				
	φ_1	φ_2	φ_3	φ_4	φ_5
200	11.62 (96)	18.69 (57)	17.85 (51)	17.85 (51)	3.63 (121)
160	13.01 (88)	19.42 (57)	18.63 (52)	18.63 (52)	3.59 (125)
120	14.94 (80)	20.60 (57)	19.90 (52)	19.90 (52)	3.59 (128)
100	16.22 (75)	21.47 (56)	20.84 (52)	20.84 (52)	3.61 (130)
80	17.85 (70)	22.63 (55)	22.10 (52)	22.10 (52)	3.65 (129)
60	20.00 (64)	24.25 (53)	23.83 (51)	23.83 (51)	3.73 (127)
40	23.08 (57)	26.65 (50)	26.37 (48)	26.37 (48)	3.85 (124)
30	25.23 (53)	28.37 (45)	28.17 (47)	28.17 (47)	3.94 (122)
20	28.10 (49)	30.66 (45)	30.55 (45)	30.93 (43)	4.06 (118)
10	32.31 (43)	34.03 (42)	34.00 (41)	35.54 (40)	4.20 (115)
1	38.87 (37)	39.15 (37)	39.15 (37)	39.41 (37)	4.41 (109)

4. Conclusion

We have developed a new method for calculating the binding energies of excitons within the framework of a variational approach. The technique is simple and straightforward to apply. Two of the great assets of the present approach are the avoidance of a series expansion, and the evaluation of rapidly convergent integrals confined to a range of integration running from 0 to 1 only. We have demonstrated the utility of the formalism by calculating the binding energies of a 1s and 2s exciton confined to an

infinitely deep potential well of varying width. The results suggest that the binding energies of the 1s and 2s exciton states can be reliably estimated in this manner via the variational approach, and also demonstrate that a choice of wavefunction that is commonly employed in the literature can result in significant underestimates of the electron-hole correlation energy for the wider wells. The extension of this method to the calculation of binding energies of excitons in a single quantum well of finite depth, or multiple quantum well systems is straightforward and will be described in a subsequent publication (Hilton *et al* 1992).

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