Polaron effects on the binding energy of a hydrogenic impurity in a semiconductor quantum well

1987 J. Phys. C: Solid State Phys. 20 5517

(http://iopscience.iop.org/0022-3719/20/33/009)

J. Phys. C: Solid State Phys. **20** (1987) 5517–5526. Printed in the UK

Polaron effects on the binding energy of a hydrogenic impurity in a semiconductor quantum well

A Erçelebi and G Süalp
Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

Received 3 October 1986, in final form 8 April 1987

Abstract. The polaron effect on the ground-state level of a hydrogenic impurity in a semiconductor quantum well is calculated as a function of the well thickness. The formulation is based on an extension of the strong-coupling polaron theory and covers the overall range of the electron–phonon coupling strength. It is observed that in a GaAs-based quantum structure the phonon-induced shift in the binding energy is smaller than that in the bulk case except for too narrow well sizes.

1. Introduction

In recent years there have been a number of studies concentrating on the effect of confinement in semiconductor quantum wells on bound states associated with hydrogenic impurities. Bastard (1981) was the first to treat the problem of a quasi-two-dimensional donor in a GaAs–GaAlAs quantum well with infinite potential barriers at the interfaces. It has been reported that an increased degree of confinement along the growth axis leads to effective potentials much deeper than that in the bulk case. Many other aspects of the same problem—such as finite barriers determined by realistic conduction band offsets at the interfaces, the effect of the non-parabolicity of the GaAs conduction band or free-carrier screening effects, for example—have been examined by various authors (Greene and Bajaj 1983, Jayakumar and Balasubramanian 1985, Brum *et al* 1984).

The contribution to the binding from the coupling of the donor electron to LO phonons has been considered by Erçelebi and Tomak (1985) within the framework of the strong-coupling polaron theory and by Degani and Hipolito (1986) in the weak-coupling limit. The latter authors include the screening effects for both the impurity potential and the electron–phonon interaction and explore the binding energy as a function of the free-electron density for various well sizes.

The case of a polaronic donor in a strictly two-dimensional approximation for the electronic charge density has been extensively investigated by Mason and Das Sarma (1986). Using perturbational, variational and Feynman path-integral techniques they have studied the corrections to the binding energy induced by electron–phonon interactions over a wide range, interpolating between the weak- and tight-binding limits.

In this work we reconsider the problem of a bound polaron in a quantum well heterostructure-type system and explore the ground-state energy as a function of the

0022-3719/87/335517 + 10 $02.50

well thickness in the overall range of the electron–phonon coupling strength. We formulate the theory in the manner proposed by Devreese *et al* (1982). The calculation is of a variational nature, and even for a small coupling constant ($\alpha \ll 1$) the procedure is to start with the strong-coupling approximation where the electron is taken to be rapidly fluctuating within a self-induced potential well built up by the correlated virtual phonons. The small-α limit is handled by a suitable modification of the adiabatic polaron state which allows the theory itself to make an extrapolation towards the weak-coupling regime.

2. Theory

The Hamiltonian we use consists of an electron attracted to a Coulomb centre located at the origin midway between the confining potential barriers of a semiconductor quantum well:

$$H = H_0 + \sum_{Q} a_Q^{\dagger} a_Q + H_{\text{e-ph}} \tag{1}$$

where

$$H_0 = -\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial}{\partial \rho}\right) - \frac{1}{\rho^2}\frac{\partial^2}{\partial \varphi^2} - \frac{\partial^2}{\partial z^2} - \frac{\beta}{r} \tag{2a}$$

$$H_{\text{e-ph}} = \sum_{Q} V_Q [a_Q \exp(\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r}) + a_Q^{\dagger} \exp(-\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r})]. \tag{2b}$$

Here we use $\hbar\omega_0$ as a unit of energy and $(\hbar/2m^*\omega_0)^{1/2}$ as a unit of length. The operators $a_Q^{\dagger}$ and a_Q respectively create and annihilate a phonon of wavevector $\boldsymbol{Q} = \boldsymbol{q} + q_z\hat{z}$ and frequency ω_0. With the normalisation volume set to unity for notational convenience, the electron–phonon interaction amplitude is $V_Q = (4\pi\alpha)^{1/2}/Q$. The dimensionless parameter $\beta = (e^2/\kappa)(2m^*/\hbar^3\omega_0)^{1/2}$ gives the strength of the Coulomb attraction screened by the static dielectric constant κ of the material.

To obtain the binding energy in the adiabatic approximation we take a Pekar-type trial *ansatz* (Pekar 1954) which is separable into the particle part φ_0 and the phonon part. We choose

$$\psi_{\text{sc}} = \varphi_0 \, \mathrm{e}^{S}|0\rangle \tag{3}$$

wherein the exponential operator e^{S}, with

$$S = \sum_{Q} V_Q \sigma_Q (a_Q - a_Q^{\dagger}) \tag{4}$$

where

$$\sigma_Q = \langle \varphi_0 | \exp(\pm \mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r}) | \varphi_0 \rangle \tag{5}$$

determines the optimal lattice deformation surrounding the electronic charge density. A further optimisation with respect to the parameters contained in φ_0 leads to the relaxed state of the system describing the composite behaviour of the electron and the surrounding polarisation field.

Under the displaced oscillator transformation $H \rightarrow \mathrm{e}^{-S} H \, \mathrm{e}^{S}$ the Hamiltonian

becomes

$$H' = H_0 + \sum_Q a_Q^\dagger a_Q + \sum_Q V_Q^2 \sigma_Q^2 - 2\sum_Q V_Q^2 \sigma_Q \cos(\boldsymbol{Q}\cdot\boldsymbol{r}) + \sum_Q V_Q(\eta_Q a_Q + \eta_Q^* a_Q^\dagger) \tag{6}$$

where

$$\eta_Q = \exp(\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r}) - \sigma_Q . \tag{7}$$

Minimisation of $\langle 0|\langle\varphi_0|H'|\varphi_0\rangle|0\rangle$ with respect to φ_0 leads to the strong-coupling result for the energy. Taking a hydrogen-like behaviour, $\varphi_0 = N\exp(-r/\sigma)$, we obtain

$$E_{\mathrm{sc}}^{(3\mathrm{D})} = -(\beta^2/4) - (5/16)\alpha\beta - (5/16)^2\alpha^2 \tag{8a}$$

for the bulk case and

$$E_{\mathrm{sc}}^{(2\mathrm{D})} = -\beta^2 - (3/8)\pi\alpha\beta - (9/256)\pi^2\alpha^2 \tag{8b}$$

when φ_0 is taken to be strictly two-dimensional. The corresponding results for a finite-width quantum structure have already been reported (Erçelebi and Tomak 1985) and we do not review them here.

We now extend the formulation to the case of weak coupling wherein what is more appropriate is the perturbation theory with $H_{\mathrm{e-ph}}$ in equation (1) taken as a perturbation. It should be noted, however, that with decreasing degree of localisation of the electron, σ_Q given by equation (5) tends to zero on average and consequently H' reduces to the starting Hamiltonian (1). One is therefore led to include a first-order correction to the trial state $\varphi_0|0\rangle$ with the last term in equation (6) being a perturbation. We then have

$$\delta\psi = \sum_Q V_Q \sum_i |i\rangle \frac{\langle i|\eta_Q^* a_Q^\dagger|\varphi_0\rangle|0\rangle}{\varepsilon_0 - \varepsilon_n - 1} \tag{9}$$

in which the energy eigenvalues ε_n ($n = 0, 1, 2, \ldots$) of the unperturbed part of H' depend on α and the lattice coordinates in an involved manner. The summation over the intermediate states can be projected out simply by replacing the energy denominator by an average quantity which in the calculation will be determined variationally. Using completeness we write

$$\delta\psi = \sum_Q V_Q g_Q \eta_Q^* a_Q^\dagger \varphi_0|0\rangle. \tag{10}$$

The trial wavefunction for the Hamiltonian H' is then extended to

$$\psi' = c\varphi_0|0\rangle + \delta\psi \tag{11}$$

where c is a normalisation constant given by

$$F(c, g_Q) = c^2 + \sum_Q V_Q^2 g_Q^2 h_Q - 1 = 0 \tag{12}$$

with

$$h_Q = 1 - \sigma_Q^2 . \tag{13}$$

In order to find the optimal fit to g_Q one has to minimise the expected value of H' in

the state (11) subject to the constraint (12). For the energy we obtain

$$E(c, g_Q) = \langle \psi' | H' | \psi' \rangle \qquad (14)$$
$$= c^2 e_0 + (1 - 2c^2)\lambda_0 + 2c \sum_Q V_Q^2 g_Q h_Q + \sum_Q V_Q^2 g_Q^2 (e_Q - f_Q + h_Q)$$

where

$$\lambda_0 = \sum_Q V_Q^2 \sigma_Q^2$$
$$e_0 = \langle \varphi_0 | H_0 | \varphi_0 \rangle$$
$$e_Q = \langle \varphi_0 | \eta_Q H_0 \eta_Q^* | \varphi_0 \rangle \qquad (15)$$
$$f_Q = 2 \sum_{Q'} V_{Q'} \sigma_{Q'} \langle \varphi_0 | \eta_Q \cos(\boldsymbol{Q}' \cdot \boldsymbol{r}) \eta_Q^* | \varphi_0 \rangle.$$

The variational procedure then requires $\partial / \partial g_Q (E - \lambda F) = 0$, with λ being a Lagrange multiplier. We find

$$g_Q / c = -h_Q [(1 - e_0 + 2\lambda_0 - \lambda) h_Q + e_Q - f_Q]^{-1} \qquad (16)$$

where

$$\lambda = \sum_Q V_Q^2 (g_Q / c) h_Q \qquad (17)$$

and the expression

$$E = e_0 - \lambda_0 + \lambda \qquad (18)$$

for the energy, which is to be minimised further with respect to φ_0.

The additive term λ, by means of which the adiabatic theory goes over to the weak-coupling regime, depends implicitly on α and β through the transcendental equation (17). For a strong enough Coulomb attraction and/or large coupling constant, λ tends to zero and the strong-coupling limit is readily obtained. However, as the coupling constant is shifted down to realistic values, such as for GaAs ($\alpha = 0.07$), the polaronic correction deviates considerably from λ_0. For a loosely bound electron the strong-coupling approximation loses its validity, since in this limit the charge density fluctuations of the electron are no longer faster than the phonon frequencies. In a perturbation theoretic calculation this feature shows up in that the corresponding perturbation series becomes poorly convergent and one needs to include the remaining terms, other than $n = 0$, as well. This is accomplished in the present formulation, however, by solving the transcendental equation (17) for the Lagrange multiplier λ.

3. Results and conclusions

For a finite-width quantum well with infinite potential barriers at $z = \pm \frac{1}{2} L$ we take the same wavefunction used by Bastard (1981) for the donor electron:

$$\varphi_0 = N \cos(\pi z / L) \exp(-r/\sigma). \qquad (19)$$

Such a choice gives a reasonable description of the ground state starting from a thin layer of the well material going over to the bulk limit. We obtain closed analytic but rather

lengthy expressions for the set of equations (15). We therefore do not present them here and are content with stating the final results only.

Before doing so, however, we would like to make a digression and summarise first the strictly two-dimensional results for completeness. In this way we achieve a means of testing the validity of the present formulation using the reasonably valid Feynman path-integral calculation adopted by Mason and Das Sarma (1986) for the same problem. We obtain

$$\begin{aligned} \lambda_0 &= \tfrac{8}{3}\pi\alpha\sigma^{-1} \\ e_0 &= \sigma^{-2} - 2\beta\sigma^{-1} \\ e_Q &= (q^2 + e_0)(1 - \sigma_Q^2) + \sigma\beta q^2\sigma_Q^2 \\ f_Q &= 2\lambda_0(1 + \sigma_Q^2) - \frac{8}{\pi}\alpha\sigma_Q \int_0^\infty \mathrm{d}q' \frac{\sigma_{Q'}}{\mu_+\mu_-^2} E(m) \end{aligned} \tag{20}$$

where

$$\sigma_Q = \left(1 + \frac{\sigma^2}{4} q^2\right)^{-3/2} \tag{21}$$

and

$$\mu_\pm = 1 + \frac{\sigma^2}{4}(q \pm q')^2 \tag{22}$$

with $E(m)$ being the complete elliptic integral of the second kind with parameter

$$m = \sin^2\left[\frac{\sigma}{\mu_+}(qq')^{1/2}\right]. \tag{23}$$

Because of the analytic complexity, the optimal fits to λ and σ have been performed numerically. Without the polaron effect ($\alpha = 0$) we obtain trivially $\lambda_0 = 0$, $\lambda = 0$ and hence $E = -\beta^2$: the two-dimensional Rydberg which is four times that for the bulk case.

Choosing $\alpha = 0.07$ and $\beta = 0.781$ for GaAs we obtain $E/\beta^2 = -1.196$. For the case of deeper binding such as in a HgTe–CdTe quantum well structure with $\alpha = 0.40$ and $\beta = 1.572$, the corresponding ratio is -1.388. The values obtained here are in perfect agreement with those derived by Mason and Das Sarma (1986) using the Feynman path-integral technique.

In table 1 we tabulate the ground-state binding energy shift $\Delta E = |E - \beta^2|$ as a function of β^2 for $\alpha = 0.07$. A comparison of our results with figure 3 of Mason and Das Sarma (1986) reveals that the formulation presented in this work yields almost identical values to those obtained by the path-integral calculation except for vanishingly small or very large β^2. In the absence of Coulomb binding with $\alpha = 0.07$ we obtain $E = -0.105$, which differs from what should be expected for a free polaron by only about 5%. The weakness of the theory in the limit $\beta \to 0$ is because a 1s-like state for the electronic

Table 1. The ground-state binding energy shift ΔE of the 2D polaronic donor as a function of β^2 for $\alpha = 0.07$.

β^2	0	0.1	0.2	0.5	1	2	3	4	5
$\Delta E(\hbar\omega_0)$	0.105	0.107	0.109	0.117	0.129	0.152	0.173	0.192	0.209

charge density becomes rather inadequate to reflect a correct description of the case where a frail Coulombic structure is dominated by the polaronic aspect. Within the framework of the same theory for a free polaron with a gaussian approximation for the variational electronic state (Erçelebi and Süalp 1987) we in fact obtain $E = -(\pi/2)\alpha \simeq 0.110$ in the weak-coupling limit. At the other extreme of rather strong Coulomb potentials ($\beta^2 \gg 1$) the path-integral theory gives somewhat underestimated values, since in this limit the hydrogen-like structure we have adopted is more appropriate than a gaussian-based approach. However, the discrepancy is still small for β^2 not too large. For $\beta^2 = 5$, for instance, the resulting deviation of the path-integral calculation from the present theory is not more than 2%.

For completeness, in figure 1 we provide a closer view of the small-β^2 regime and compare our results with the approximation based on the effective mass argument—$\Delta E = (\pi/2)\alpha + (\pi/8)\alpha\beta^2$ (see Mason and Das Sarma 1986)—which proves to work well for small α and for small β^2 (i.e., $R_{2D} \ll \hbar\omega_0$) . We once again observe a very close agreement between the two approaches except when $\beta^2 \ll 1$ and $\beta^2 \gg 1$. The disagreement in the small-β^2 limit is attributed to the present calculation for the reasons given above, whereas the deviation for comparatively stronger Coulomb binding is essentially because the approximate effective mass formula becomes no longer equivalent to an electron orbiting together with its concomitant lattice deformation (i.e., the polaron state undergoes a change from a nearly free to a relatively localised one).

Having reviewed the purely two-dimensional polaronic donor, we now continue with

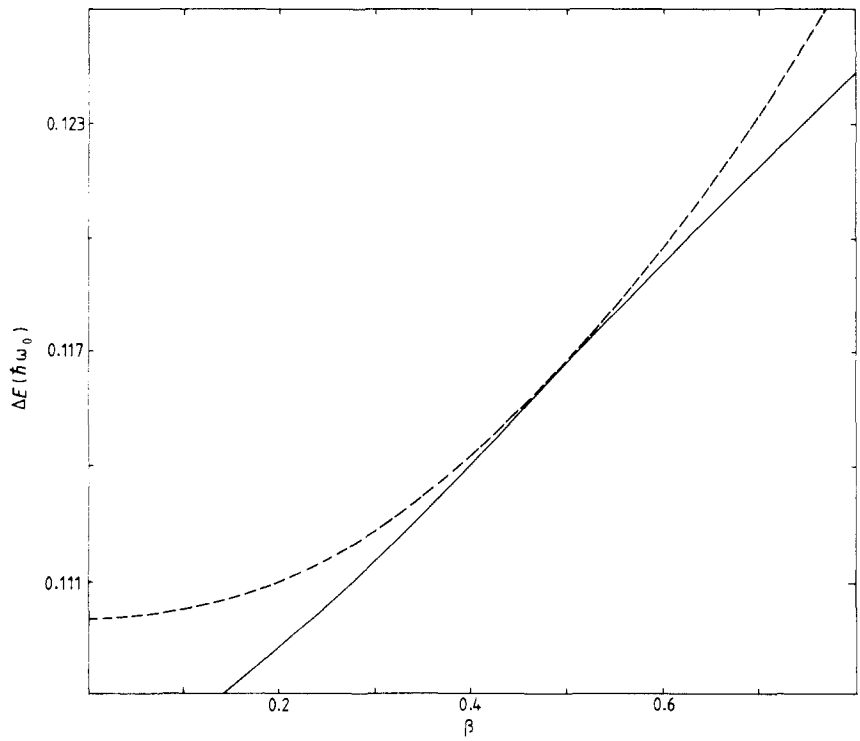

Figure 1. The polaronic shift ΔE plotted against β in the 2D approximation. The full and broken curves display the results of the present formulation and of the approximation based on the effective mass argument respectively. $\alpha = 0.07$.

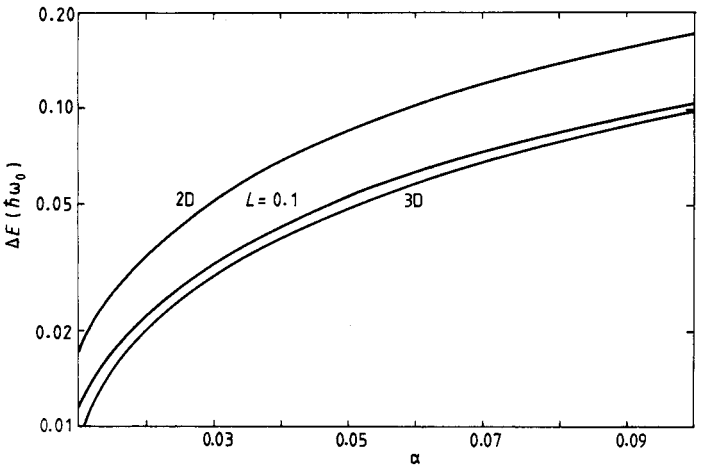

Figure 2. The α dependence of ΔE for the 3D and 2D cases as well as for $L = 0.1$ (in units of the unperturbed 3D Bohr radius). $\beta = 0.781$.

our main theme and present an overview of the polaron effect in a finite-width quantum well with α, β and L being retained as free parameters. In figure 2 we provide an explicit plot of the α dependence for the phonon-induced shift $\Delta E = |E(\alpha) - E(\alpha = 0)|$ in the binding energy. We take $\beta = 0.781$ as for GaAs and display the general trend for two and three dimensions as well as for $L = 0.1$ (in units of the unperturbed three-dimensional Bohr radius, $a_{3D} = 2\beta^{-1}$).

A more complete representation of the behaviour of the system is given in table 2 where we tabulate an array of values for ΔE over various well thicknesses ranging between the two-dimensional and bulk limits with $\alpha = 0.02, 0.05, 0.1, 0.2$ and $\beta^2 = 0.1$, 2, 10. As expected the polaronic contribution to the binding increases in general with increasing degree of confinement (i.e., with increasing β^2 or L^{-1} as well as with increasing α).

It should be evident that the three parameters (α, β and L) characterising the system do not all enter the problem in an independent way but together play a somewhat involved and interrelated role in the binding. In fact a careful examination of the various columns in table 2 (as well as figure 3) reveals that ΔE undergoes rather interesting types of variations when we vary L. We observe that, for comparatively large values of β^2, ΔE increases monotonically as the dimensionality is reduced from three to two (cf. the curve for $\beta^2 = 10$ in figure 3). Such a feature clearly originates from the fact that, with decreasing L, the electron is forced to orbit in two dimensions and the wavefunction is squeezed onto the Coulomb centre, resulting in stronger binding and hence an enhancement in the polaron effect.

For weaker binding (small β^2) the behaviour is rather different. Going from the bulk case to the two-dimensional limit there comes about a competitive interrelation between whether the charge distribution (and the lattice deformation) will be pushed onto the impurity centre or will expand to relax itself in the transverse directions. Starting from $L \gg 1$ the effect of the expansion dominates first, causing the polaron effect to decrease. Meanwhile, with the contracting dimension the electronic cloud experiences an increasingly large pressure and therefore, after a certain well width, the degree of localisation of the electron–phonon system starts to increase, leading to larger polaronic con-

Table 2. The ground-state binding energy shift ΔE for various well widths ranging between the 2D and bulk limits. (The well width L is given in units of the unperturbed 3D Bohr radius, $2\beta^{-1}$).

	$\Delta E(\hbar\omega_0)$			
	$\alpha = 0.02$	$\alpha = 0.05$	$\alpha = 0.10$	$\alpha = 0.20$
$L\ (2\beta^{-1})$	$\beta^2 = 0.1$			
2D	0.0311	0.0771	0.1517	0.2960
0.1	0.0173	0.0435	0.0873	0.1731
0.2	0.0165	0.0415	0.0838	0.1679
0.5	0.0148	0.0373	0.0759	0.1551
1	0.0134	0.0334	0.0682	0.1411
2	0.0131	0.0315	0.0620	0.1268
3D	0.0194	0.0480	0.0944	0.1840
	$\beta^2 = 2$			
2D	0.0435	0.1090	0.2189	0.4412
0.1	0.0332	0.0827	0.1654	0.3324
0.2	0.0305	0.0760	0.1520	0.3056
0.5	0.0256	0.0633	0.1264	0.2543
1	0.0219	0.0534	0.1059	0.2121
2	0.0197	0.0466	0.0906	0.1786
3D	0.0206	0.0514	0.1024	0.2035
	$\beta^2 = 10$			
2D	0.0793	0.1988	0.3991	0.8042
0.1	0.0657	0.1641	0.3286	0.6605
0.2	0.0607	0.1513	0.3028	0.6085
0.5	0.0502	0.1247	0.2491	0.4998
1	0.0411	0.1018	0.2026	0.4093
2	0.0331	0.0821	0.1627	0.3237
3D	0.0266	0.0665	0.1331	0.2670

tributions to the binding (cf. the curve for $\beta^2 = 0.1$ in figure 3). For comparatively stronger Coulomb attraction this salient feature becomes less prominent and does not even show up, since the starting state of the system will already be a localised one.

We now confine our discussions to a GaAs-based quantum structure and give the relevant results in table 3. We at once observe that ΔE increases by a fairly large factor of about 1.74 when the dimensionality is reduced from three to two. Such an enhancement in the overall polaron effect should not be misleading, mainly because the purely two-dimensional limit of the model is only interesting from a formal point of view and obviously cannot produce a reliable physical picture. For actual well widths of interest the polaronic corrections to the energy are much lower than those indicated by the two-dimensional approximation. In going from the bulk case to $L = 20$ Å, for instance, the increase in ΔE is only about 1%. For thicker well widths the situation is even more drastic. In contrast to what is usually expected, the phonon contributions to the ground level do not become enhanced but are reduced (by about 6% for $L = 50$ Å and by 8% for $L = 100$ Å) compared with the three-dimensional case. The reason for such a large discrepancy between our finite-width results and those of Mason and Das

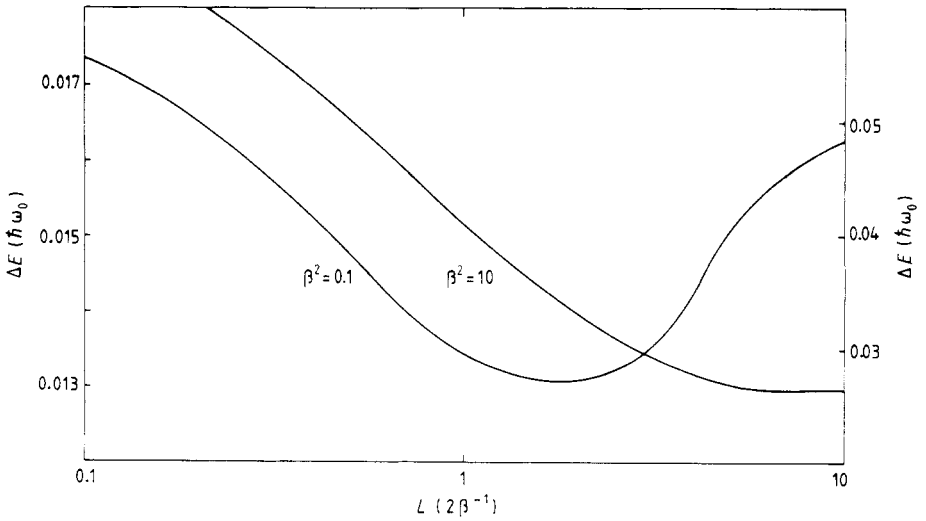

Figure 3. The ground-state binding energy shift ΔE plotted against L (in units of the unperturbed 3D Bohr radius). The energy scale on the left (right) is for $\beta^2 = 0.1$ (10). $\alpha = 0.02$.

Sarma (1986) is essentially due to their interpolation scheme based on the effective mass argument, which strictly requires the free-polaron energy to be totally separable. Although the approximate effective mass approach marginally holds true for GaAs in purely two and three dimensions, this does not seem to be the case for a finite-width quantum well. It should be noted that the energy expression (18) involves implicitly some fraction of the bound-state energy of the free polaron, which itself is $-\alpha$ in three dimensions and $-(\pi/2)\alpha$ in two dimensions. In fact the percentage of the free-polaron energy which actually plays a significant role in the binding and the percentage which can be regarded as separable depend on α and β, and also on L. With parameter values appropriate to GaAs, the effective mass formula for the two-dimensional case is only approximately valid, yielding a slightly overestimated polaron effect, $\Delta E \simeq 0.127$ (cf. figure 1). The corresponding three-dimensional value is $\Delta E = \alpha + (\alpha/6)(\beta^2/4) \simeq 0.072$, which is inevitably larger than that obtained in the present calculation ($\Delta E \simeq 0.069$). The discrepancy is, however, rather small in both extremes of the well size. With L introduced into the model as a further parameter the discrepancy grows larger and, starting from either the two-dimensional or the bulk limit, ΔE calculated in this way rapidly becomes much smaller than the approximate results of the approach based on the effective mass argument. As we pointed out earlier in this section, the well width does not play its role independently in the binding but also seriously affects the contributions of the remaining parameters α and β, therefore altering the qualitative aspects of the effective mass argument. In our opinion it is this interrelation among α, β and L which

Table 3. ΔE as a function of L for a GaAs-based quantum well structure ($\beta = 0.781$, $\alpha = 0.07$).

L (Å)	2D	10	20	50	100	200	3D
$\Delta E(\hbar\omega_0)$	0.1195	0.0736	0.0696	0.0650	0.0636	0.0612	0.0688

sets the results of the present theory apart from the interpolation scheme of Mason and Das Sarma (1986).

In conclusion, we have formulated the problem of a bound polaron confined in a semiconductor quantum well structure using the variational approach proposed by Devreese *et al* (1982). We observe that for not too strong Coulomb potentials the polaron contribution to the binding goes through a minimum as the well width is varied between the bulk and two-dimensional limits. What is more unusual is that the phonon-induced shift in the energy levels may be even smaller than in the bulk except for narrow quantum wells. It should be emphasised that this striking feature applies to the most commonly studied GaAs-based quantum structure.

References

Bastard G 1981 *Phys. Rev.* B **24** 4714
Brum J A, Bastard G and Guillemot C 1984 *Phys. Rev.* B **30** 905
Degani M H and Hipolito O 1986 *Phys. Rev.* B **33** 4090
Devreese J, Evrard R, Kartheuser E and Brosens F 1982 *Solid State Commun.* **44** 1435
Erçelebi and Süalp G 1987 *J. Phys. Chem. Solids* **48** 739
Erçelebi A and Tomak M 1985 *Solid State Commun.* **54** 883
Greene R L and Bajaj K K 1983 *Solid State Commun.* **45** 825
Jayakumar K and Balasubramanian S 1985 *Phys. Rev.* B **32** 6904
Mason B A and Das Sarma S 1986 *Phys. Rev.* B **33** 8379
Pekar S I 1954 *Untersuchungen über die Elektronentheorie der Kristalle* (Berlin: Akademie)