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Hydrogenic impurity ground state in quantum well: the envelope function revisited

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Abstract. We present a new variationnal method for calculating the ground state energy of an electron bound to an impurity located in a quantum well. This method relies on an envelope function which is determined *exactly* from a formal minimization procedure. The obtained energies are lower by as much as 10% than the ones found by the widely used free electron envelope function. Their large width limits are reached with exponentially small corrections as they should. We also find that, except for narrow wells, the shape of these exact envelope functions strongly depends on the impurity position, being consequently quite different from the usual free electron ones. In order to discuss the improvements brought by our new procedure in the most striking way, we have used a model semiconductor quantum well with infinite barrier height and simplified band structure. Extensions can be made to finite barrier and more realistic band structures, following the same technique.

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In this paper, we propose a new variationnal procedure to determine the ground state energy of an electron bound to an impurity, when this impurity is located inside a quantum well. Although this problem has been studied for a long time [1–8], we have been led to reconsider it because the solution proposed up to now is potentially not accurate enough to be used in the determination of the exciton dead layer we are going to present in a forthcoming paper. Indeed, in this dead layer problem, we will have to use an energy analogous to the ground state energy of an electron bound to an impurity, and which has to be valid up to $(a_x/L)^3$ at least in the large L limit, a_x being the Bohr radius and L the well width. Unfortunately, while the previous procedure [1] of course gives the correct limiting values for small and large L, it incorrectly gives the way the energy approaches its large L value, merely because it was essentially designed to describe narrow wells. Specifically the corrections are quadratic instead of exponentially small as they should. This dramatically affects the energy of an exciton in a large width quantum well since incorrect quadratic corrections add a spurious contribution to the exciton center of mass energy. This urged us to study again the problem of an electron bound to an impurity in order to find more accurate solutions.

The new variationnal procedure presented here gives an energy somewhat lower than the one found previously and has the required property of reaching its large L value with exponentially small corrections. This procedure is conceptually somewhat different from the previous one since it relies on the exact determination of the optimum envelope function [2,9] of an electron bound to an impurity located in a quantum well. We show that, except for narrow wells, this envelope function crucially depends on the impurity position, being quite different from the usual free electron one. *As this free electron envelope function is by now a widely used concept, it is of major importance to realize that it can be indeed so far from the exact one*: once more we do see that wave functions are much more tricky to obtain correctly than energies and that rather bad ones can still give pretty good energy values.

In order to explain our procedure and to compare it to the previous one in a simple and efficient way, we have taken the case of the simplest model semiconductor quantum well, with infinite barrier height and isotropic effective mass. The solutions then depend on two parameters only: the well width and the impurity position, so that the comparison of the two procedures is quite easy. We wish to stress that, although somewhat heavier numerically, our new procedure can also be used for more realistic quantum wells [10]. In particular its extension to finite barrier height will be the subject of a forthcoming note.

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The paper is organized as follows:

- In Section 1, we present the problem and briefly recall the expected limiting behaviors for wide and narrow quantum wells.
- In Section 2, we consider a trial function which is the product of a function of the electron position z inside the well by a function of the electron distance to the impurity located at

$$\begin{aligned} \mathbf{r}_i &= (0,0,z_i) \\ \langle \mathbf{r}|\varphi\rangle &= f(z)\, g(|\mathbf{r}-\mathbf{r}_i|). \end{aligned} \tag{1}$$

  This form of trial function is the only one we know for which the boundary condition $\langle r|\varphi\rangle = 0$ on the well borders $z = \pm L/2$ (or the well sample in the case of a finite barrier height), can be enforced in a tractable way for any (x,y). By using for $g(r')$ the following function:

$$g(r')\exp(-r'/\lambda a_x) \tag{2}$$

  which properly reproduces the known limiting cases, we show how one can easily recover the energies in the large L limit. In his pioneering work on impurity in quantum wells, Bastard [1] has used this type of trial function with, for *f(z)*, the free electron envelope function $f(z) = \cos\pi z/L$ in order to get the ground state binding energy for intermediate well widths. We recall his main results and explicitly show that this free electron envelope function generates undesirable $(a_x/L)^2$ corrections in the large L limit.
- In Section 3, we formally determine the optimal *f(z)*, *i.e.* the $f(z)$ which gives the lowest energy for the set of $g(r')$ given in equation (2). We find that, for a given λ, the optimal $f(z)$ is solution of a second order differential equation which can be solved analytically in terms of degenerate hypergeometric functions [11]. From a minimization procedure with respect to λ, we finally get the ground state energy $\varepsilon(z_i, L)$ and the envelope function $f(z)$ as a function of the impurity location z_i and well width L, for any z_i and L.
- In a last section, we discuss the results and compare them to the previous procedure which uses the usual free electron envelope function.

1 The problem and its expected solutions for wide and narrow wells

We consider a quantum well extending between $-L/2$ and $L/2$ and an impurity located at $\mathbf{r}_i = (0,0,z_i)$ inside the well. The electron Hamiltonian in the presence of the impurity reads $H = p^2/2\mathrm{m} - e^2/|\mathbf{r}-\mathbf{r}_i| + U(z)$ where the confinement potential $U(z)$ is given by $U(z) = 0$ if $-L/2 < z < L/2$ and $U(z) = U_0$ otherwise. In the following we will assume $U_0 = \infty$ for simplicity. However we will on occasions indicate the modifications brought by a finite U_0. In the following, it will appear appropriate to use the variable $\mathbf{r}' = \mathbf{r} - \mathbf{r}_i$ instead of $\mathbf{r}$. The corresponding Hamiltonian then reads

$$H = \frac{p^2}{2m} - \frac{e^2}{r'} + v_{z_i}(z') \tag{3}$$

where the confinement potential is now given by $v_{z_i}(z') = 0$ if $d_- < z' < d_+$ and $v_{z_i}(z') = \infty$ otherwise, with $d\pm = \pm L/2 - z_i$. Due to the well confinement, the H eigenstates $\langle \mathbf{r}|\varphi\rangle = \varphi(x,y,z)$ are such that $\varphi(x,y,\pm L/2) = 0$ for infinite barriers. As this boundary condition must be fulfilled for any (x,y), it corresponds to an infinite number of boundary conditions. One can enforce this equation in a tractable way by using a trial function having a function of z as a prefactor, namely $\langle \mathbf{r}|\varphi\rangle \approx f(z)g(\mathbf{r})$. The boundary condition is then satisfied by requiring $f(\pm L/2) = 0$. As the quality of a trial function strongly relies on the adequacy of its choice, which usually results from a precise analysis of the expected limiting values, we now briefly recall what are the electron ground states in the small and large L/a_x limits.

1.1 Small well width L $\ll$ a$_x$

For narrow quantum wells, the Coulomb interaction holds the electron close to the impurity in the (x,y) direction, while it has little effect on the z motion due to the strong confinement in the z direction. We thus expect a contribution to the ground state binding energy equal to $-4R_x$, with $R_x = me^4/2\hbar^2 = \hbar^2/2ma_x^2$, coming from the 2D motion in the (x,y) plane and a $\hbar^2\pi^2/2mL^2$ contribution from the z motion inside the well. Consequently the ground state energy of an electron bound to an impurity in a narrow quantum well should behave as $R_x[\pi^2(a_x/L)^2 - 4 + \ldots]$ in the small (L/a_x) limit; the corresponding wave function $\cos(\pi z/L)\exp[-2(x^2+y^2)^{1/2}/a_x]$ is basically independent of the impurity position z_i inside the well since the relevant variable $(z-z_i)/a_x$ stays always very small.

1.2 Large well width L $\gg$ a$_x$

On the opposite, for large well width, the ground state energy drastically depends on the impurity position.

a) *Impurity far from the walls*

When the impurity is at a distance large from the walls compared to a_x, the electron which is forced to stay close to the impurity by Coulomb interaction does not feel these walls; the system looks like a 3D hydrogen atom in vacuum. Its ground state wave function $\exp(-r'/a_x)$ corresponds to the $(n = 1, l = 0 = m)$ hydrogenoïd state and its energy is $(-R_x)$ with exponentially small corrections of the order of e^{-2L/a_x} which come from the probability for the electron to be on the wall.

b) *Impurity just on the wall*

When the impurity gets close to the wall, the ground state ($n = 1, l = 0 = m$) wave function has to distort in order to satisfy the boundary condition $\varphi(x, y, \pm L/2) = 0$. Just on the wall, it is easy to check that, the wave function $z' \exp(-r'/2a_x)$ which corresponds to the ($n = 2, l = 1, m = 0$) hydrogenoïd state is eigenfunction of H, and fulfills this boundary condition, the corresponding energy being $(-R_x/4)$.

1.3 Expected solutions

We thus conclude that, in the above three limiting cases for which we easily know the answer, the wave function is well reproduced by $\langle \mathbf{r}|\varphi\rangle = f(z)\exp(-|\mathbf{r} - \mathbf{r}_i|/\lambda a_x)$ with $\lambda = 1/2$ for narrow wells and $\lambda = 1$ or 2 for large wells depending on the impurity position, far or close to the wall respectively.

If we now consider the energy, it diverges for small L due to the confinement in the z direction. This is why one often introduces a quantity which stays finite for all L by extracting the small L diverging contribution of $\varepsilon(z_i, L)$. This quantity, known as the "electron binding energy" $\varepsilon_{\mathrm{B}}(z_i, L)$ is defined by

$$\varepsilon(z_i, L) = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2} + \varepsilon_{\mathrm{B}}(z_i, L). \tag{4}$$

With increasing L/a_x this binding energy goes from $(-4R_x)$ to $(-R_x)$ when the impurity is far from the wall, and from $(-4R_x)$ to $(-R_x/4)$ when the impurity is on the wall. Let us however stress that, as $\varepsilon(z_i, L \to \infty)$ reaches its asymptotic value ($-R_x$ or $-R_x/4$) with exponentially small corrections, ε_{B} reaches the same asymptotes much more slowly, the corrections being of the order of $(a_x/L)^2$; so that the quantity $\varepsilon_{\mathrm{B}}(z_i, L)$ is somewhat inappropriate if we are interested in rather large quantum wells.

2 Expected properties of the trial function

We want to determine the ground state energy of the Hamiltonian (3), *i.e.* the minimum of $\varepsilon(z_i, L) = \langle\varphi|H|\varphi\rangle/\langle\varphi|\varphi\rangle$. Introducing the trial function given by equation (1) and making by part integrations we find:

$$\langle\varphi|H|\varphi\rangle = \frac{\hbar^2}{2m}\int \mathrm{d}^3r \left[(fg')^2 - g^2\left(ff'' + \frac{2}{r'a_x}f^2\right)\right] \tag{5}$$

where f' and f'' are the derivatives of f. If we restrict ourselves to the $g(r')$ functions given by equation (2), we get

$$\langle\varphi|H|\varphi\rangle = R_x\left[\frac{1}{\lambda^2} - a_x^2\int \mathrm{d}^3r \mathrm{e}^{-2r'/\lambda a_x}\left(ff'' + \frac{2}{r'a_x}f^2\right)\right] \tag{6}$$

with the normalization $\langle\varphi|\varphi\rangle = 1$. We perform the integration over (x, y) in equation (6) and in the normalization condition. By writing

$$f(z) = \sqrt{\frac{1}{2\pi}\left(\frac{2}{\lambda a_x}\right)^3}\,\hat{f}\left(\frac{2(z - z_i)}{\lambda a_x}\right) \tag{7}$$

(the a_x factors come from dimensional arguments while the other prefactors are just introduced for simplifying the following algebra), the normalization condition reads

$$1 = \int_{D_-}^{D_+} \mathrm{d}u(1 + |u|)\mathrm{e}^{-|u|}\hat{f}^2(u) \tag{8}$$

while the Hamiltonian average value equation (6) is now given by

$$\langle\varphi|H|\varphi\rangle = \frac{R_x}{\lambda^2}\left\{1 - 4\int_{D_-}^{D_+} \mathrm{d}u\, \mathrm{e}^{-|u|}\left[(1 + |u|)\hat{f}\hat{f}'' + \lambda\hat{f}^2\right]\right\} \tag{9}$$

the boundary conditions being $\hat{f}(D_\pm) = 0$ with $D_\pm = (2/\lambda a_x)(\pm L/2 - z_i)$. Due to the exponentials, the dominant contributions to these integrals come from $|u| \leq 1$. For a given λ, the Hamiltonian average value is thus controlled by the shape of $\hat{f}(u)$ for $|u|$ close to 0, *i.e.* the shape of $f(z)$ in the neighbourhood of the impurity.

a) We know that, for impurity infinitely far from the wall, the exact solution corresponds to $\hat{f}(u)$ constant. For $|D_\pm| \gg 1$, we thus expect $\hat{f}(u)$ to be constant $\hat{f}(u) \approx b_0$ for $|u| < \ell$, the necessary decrease of $\hat{f}(u)$ to reach $\hat{f}(D_\pm) = 0$ being pushed away to $|u| \geq \ell$ (with ℓ being a fraction of L/a_x). The constant b_0 can then be determined by the normalization condition equation (8) which gives $b_0 = 1/2$. If we insert this $\hat{f}$ into equation (9) we get

$$\langle\varphi|H|\varphi\rangle = \frac{R_x}{\lambda^2}\left[1 - 4\int_{-\infty}^{\infty} \mathrm{d}u\, \mathrm{e}^{-|u|}\lambda b_0^2\right] = R_x\left(\frac{1}{\lambda^2} - \frac{2}{\lambda}\right). \tag{10}$$

From it, we find that the minimum energy corresponds to $\lambda^* = 1$, so that this minimum is $-R_x$ as expected for an impurity far away from the walls. The corrections to this $(-R_x)$ value come from $|u|$ larger than ℓ. They are thus exponentially small. If, instead of $\hat{f}(u)$ constant, we try a somewhat more elaborate $\hat{f}(u) = b_0 + b_1 u + b_2 u^2$, we can show that the minimum energy does correspond to $b_1 = b_2 = 0$, *i.e.* $\hat{f}(u)$ indeed constant.

b) When the impurity is on the wall, and the other wall is infinitely far away, we know that the exact solution corresponds to the ($n = 2$, $l = 1$, $m = 0$) hydrogenoïd state, *i.e.* $\hat{f}(u) = a_1 u$. If we use this solution for $0 < u < \ell$ and push the necessary decrease of $\hat{f}(u)$ to reach $\hat{f}(D_+) = 0$ at u close to $L/\lambda a_x$, the normalization condition equation (8)

$$B=\frac{1+\dfrac{C}{A}+\dfrac{1-A}{A}\left(\dfrac{\mathrm{e}^{-D_+}+\mathrm{e}^{D_-}}{2}\right)}{1+\dfrac{C}{A^2}+\dfrac{1-A^2}{A^2}\left(\dfrac{\mathrm{e}^{-D_+}+\mathrm{e}^{D_-}}{2}\right)+\dfrac{1-A}{A}\left(\dfrac{D_+\mathrm{e}^{-D_+}-D_-\mathrm{e}^{D_-}}{4}\right)} \tag{13}$$

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leads to $a_1^2=1/8$. So that equation (9) gives

$$\begin{aligned}\langle\varphi|H|\varphi\rangle &= \frac{R_x}{\lambda^2}\left[1-4\int_0^\infty \mathrm{d}u\,\mathrm{e}^{-u}\lambda a_1^2u^2\right]\\ &= R_x\left(\frac{1}{\lambda^2}-\frac{1}{\lambda}\right).\end{aligned} \tag{11}$$

Its minimum, obtained for $\lambda^*=2$, corresponds to $-R_x/4$, the associated wave function being

$$\sqrt{\frac{1}{2\pi}\left(\frac{2}{2a_x}\right)^3}\,\frac{1}{\sqrt{8}}\,\frac{2z'}{2a_x}\mathrm{e}^{-r'/2a_x}=\frac{1}{2\sqrt{\pi}a_x^{3/2}}\mathrm{e}^{-r'/2a_x}\frac{z'}{a_x} \tag{12}$$

as expected for the ($n=2$, $l=1$, $m=0$) hydrogenoïd state. As the corrections to this ($-R_x/4$) energy come from the $u\geq\ell$ region, they are, here again, exponentially small. If we try to add some curvature by using $\hat{f}(u)=a_1u+a_2u^2$, we can check that the lowest energy does correspond to $a_2=0$.

c) The same procedure allows to get the way the energy reaches its $-R_x/4$ value when the impurity approaches the wall. Indeed, for an impurity at δ from it, *i.e.*, for $z_i=-L/2+\delta$, we have $d_-=-\frac{L}{2}-\left(-\frac{L}{2}+\delta\right)=-\delta$ while $d_+=L-\delta\approx L$. In order to fulfill the boundary condition $f(d_-)=0$, we are led to take $\hat{f}(u)$ as $\hat{f}(u)=a_1(u+\hat{\delta})$ with $\hat{\delta}=2\delta/\lambda a_x$. The normalization condition equation (8) gives $a_1^2=\left(1-3\hat{\delta}/4\right)/8$ while the Hamiltonian average value reads $\langle\varphi|H|\varphi\rangle=R_x[(1-\delta/2a_x)/\lambda^2-1/\lambda]$. At first order in δ/a_x, its minimum value corresponds to $\lambda^*=2-\delta/a_x$, *i.e.* $\langle\varphi|H|\varphi\rangle_{\min}=R_x[-1/4-\delta/8a_x]$ which shows that the energy ($-R_x/4$) is reached with a ($-R_x/8a_x$) slope. This analytical result is in very good agreement with the numerical calculations presented below. It is possible to show that this slope is unchanged if one adds some curvature to the $\hat{f}(u)$ function, *i.e.* if one uses $\hat{f}(u)=a_1(u+\hat{\delta})+a_2(u+\hat{\delta})^2$.

d) In order to find the energy for intermediate z_i one can think to follow Bastard [1] and use for $f(z)$ a function proportional to the free electron envelope function $\cos\pi z/L$, as it fulfills the boundary conditions $f(\pm L/2)=0$. In agreement with his equations (7) and (14), we then get the Hamiltonian average value equation (9) as $\langle\varphi|H|\varphi\rangle=R_x[(1/\lambda^2)+\eta^2-2B/\lambda]$ with $\eta=\pi a_x/L$ identical to his (k_1a_x) and

see equation (13) above

where we have set $A=1+\lambda^2\eta^2$ and $C=\cos 2k_1z_i$.

The main advantage of this free electron $f(z)$ function is to generate an analytical expression for the Hamiltonian average value which has just to be numerically minimized with respect to λ, the deduced energy having indeed the correct limiting values for small and large L and for $z_i=0$ and $z_i=\pm L/2$.

We now show that, unfortunately, this energy does not have the property required for using it in the exciton dead layer problem, namely it does not reach its asymptotic values in the large L limit faster than $(a_x/L)^3$.

(i) When the impurity is far from the walls, $|D_\pm|$ is large and equation (13) gives $B=A(A+C)/(A^2+C)$ so that we get

$$\langle\varphi|H|\varphi\rangle=R_x\left[\frac{1}{\lambda^2}+\eta^2-\frac{2}{\lambda}\left(1+C\frac{\eta^2\lambda^2}{C+(1+\eta^2\lambda^2)^2}\right)\right]. \tag{14}$$

To lowest order in η, its minimum corresponds to $\lambda^*\approx 1+\eta^2C/(C+1)$, so that the energy is given by $R_x[-1+\eta^2(1-C)/(1+C)+O(\eta^4)]$. We thus see that, except for $C=1$, *i.e.* $z_i=0$, the corrections are in η^2, *i.e.* in $(a_x/L)^2$.

(ii) When the impurity is just on the walls, *i.e.* for $z_i=L/2$, we have $C=-1$ and $D_+=0$. For $|D_-|$ large, B reduces to $B=A/(A+1)$ so that we find

$$\langle\varphi|H|\varphi\rangle=R_x\left[\frac{1}{\lambda^2}+\eta^2-\frac{2}{\lambda}\left(\frac{1+\eta^2\lambda^2}{2+\eta^2\lambda^2}\right)\right]. \tag{15}$$

In the small η limit, its minimum which is reached for $\lambda^*\approx 2+4\eta^2$, now corresponds to $R_x[-1/4+O(\eta^4)]$. We thus conclude that, when taking $f(z)$ to be $\cos(\pi z/L)$ in equation (9), the asymptotic values of the energy are reached with $(a_x/L)^2$ corrections, except just at the center or at the borders of the well, the corrections being then in $(a_x/L)^4$. In any case, they are much larger than the exponentially small corrections we expect. We will show that one can trace these spurious terms to the fact that $\cos(\pi z/L)$ is not flat enough in the neighbourhood of the impurity when compared to the exact $f(z)$.

3 Exact determination of the optimum $\hat{f}$

We now determine analytically the function $\hat{f}$ which minimizes $\langle\varphi|H|\varphi\rangle$ as given in equation (9) provided that the normalization condition (8) is fulfilled. Such an $\hat{f}$ should verify $0=\delta[\langle\varphi|H|\varphi\rangle-\chi\langle\varphi|\varphi\rangle]$ with χ being a Lagrange multiplier. Using equations (8, 9), this gives

$$\begin{aligned}0=\int_{D_-}^{D_+}\mathrm{d}u\,\mathrm{e}^{-|u|}\Big[&(1+|u|)\hat{f}\delta\hat{f}''\\ &+\Big\{(1+|u|)\hat{f}''+2\left(\lambda-\chi'(1+|u|)\right)\hat{f}\Big\}\delta\hat{f}\Big]\end{aligned} \tag{16}$$

with $\chi' = -\chi\lambda^2/4R_x$. We can rewrite the $\delta\hat{f}''$ part of this integral in terms of $\delta\hat{f}$ by integrating twice by part as, for any $h(u)$ function, we have

$$\int_{D_-}^{D_+} \mathrm{d}u\, h\hat{f}\delta\hat{f}'' = -\int_{D_-}^{D_+} (h\hat{f})'\,\delta\hat{f}' = \int_{D_-}^{D_+} (h\hat{f})''\,\delta\hat{f} \quad (17)$$

provided that $\delta\hat{f}'(D_\pm)$ is finite and $\delta\hat{f}(D_\pm) = 0$, as enforced by the boundary conditions $\hat{f}(D_\pm) = 0$. If we use the above equation for $h(u) = (1+|u|)\mathrm{e}^{-|u|}$ equation (16) becomes

$$\begin{aligned} 0 = \int_{D_-}^{D_+} \mathrm{d}u\, \mathrm{e}^{-|u|} \big[& 2(1+|u|)\hat{f}'' - 2u\hat{f}' \\ & + (2\lambda - 2\chi' - 1 + (1-2\chi'))\,|u|\big]\,\delta\hat{f}. \end{aligned} \quad (18)$$

As equation (18) has to be verified for any $\delta\hat{f}$, we get the differential equation satisfied by the optimal $\hat{f}$ by requiring the bracket in equation (18) to be zero

$$(1+|u|)\hat{f}'' - u\hat{f}' + \left[\lambda - \chi' - \frac{1}{2} + \left(\frac{1}{2} - \chi'\right)|u|\right]\hat{f} = 0. \quad (19)$$

Before solving this differential equation, let us note that $\langle\varphi|H|\varphi\rangle$ for such $\hat{f}$ writes extremely simply in terms of χ'. Indeed, if we insert the value of $(1+|u|)\hat{f}''$, as given by equation (19), into equation (9), we get $\langle\varphi|H|\varphi\rangle = R_x(1-4I)/\lambda^2$ where I, defined by

$$I = \int_{D_-}^{D_+} \mathrm{d}u\, \mathrm{e}^{-|u|} \left\{ u\hat{f}\hat{f}' + \left[\chi' + \frac{1}{2} + \left(\chi' - \frac{1}{2}\right)|u|\right]\hat{f}^2 \right\} \quad (20)$$

is nothing but χ': indeed an integration by part of the $\hat{f}\hat{f}'$ term gives

$$\int_{D_-}^{D_+} \mathrm{d}u\, \mathrm{e}^{-|u|}\hat{f}\hat{f}' = \frac{1}{2}\int_{D_-}^{D_+} \mathrm{d}u(|u|-1)\mathrm{e}^{-|u|}\hat{f}^2. \quad (21)$$

So that I reads

$$I = \chi' \int_{D_-}^{D_+} \mathrm{d}u\, \mathrm{e}^{-|u|}(1+|u|)\hat{f}^2 = \chi' \quad (22)$$

due to the normalization condition equation (8). We thus find

$$\langle\varphi|H|\varphi\rangle = -R_x\,\nu^2/\lambda^2 \quad (23)$$

where ν is related to the Lagrange multiplier χ through $\nu^2 = 4\chi' - 1 = -(1 + \chi\lambda^2/4R_x)$. Note that a negative energy corresponds to ν real and a positive energy to ν imaginary.

This simple expression was actually to be expected. Indeed, except for the constant term R_x/λ^2 in equation (9), we essentially deal with an Hamiltonian problem. Precisely, after a single integration by parts, we can rewrite equation (9) as:

$$\begin{aligned} \langle\varphi|H|\varphi\rangle - \frac{R_x}{\lambda^2} = \frac{4R_x}{\lambda^2} & \int \mathrm{d}u\, \mathrm{e}^{-|u|} \\ \times & \left[(1+|u|)\hat{f}'^2 + \left(\frac{1}{2} - \lambda - \frac{|u|}{2}\right)\hat{f}^2\right] \equiv \langle\hat{f}|H|\hat{f}\rangle \end{aligned} \quad (24)$$

(the change of variable $\mathrm{d}v = \mathrm{d}u/[\mathrm{e}^{-|u|}(1+|u|)]$ would make the similarity more obvious). Our differential equation, resulting from the minimization with respect to $\hat{f}$, is then equivalent to solving $H|\hat{f}\rangle = \chi|\hat{f}\rangle$. Once a solution, satisfying the normalization condition equation (8), namely $\langle\hat{f}|\hat{f}\rangle = 1$, is known, the energy simply results from $\langle\hat{f}|H|\hat{f}\rangle = \chi\langle\hat{f}|\hat{f}\rangle = \chi$ which is just the result found in equation (23). This remark allows to see that our procedure can be extended quite easily to quantum wells with finite barrier height: one has just to use the corresponding Hamiltonian with finite U_0.

The differential equation (19) for the optimal $\hat{f}$ is solved in the Appendix; its general solution is found to be

$$\hat{f}(u) = a\,\mathcal{M}(1+|u|) + b\,\mathcal{U}(1+|u|) \quad (25)$$

where the functions $\mathcal{M}(v)$ and $\mathcal{U}(v)$ write in terms of the confluent hypergeometric functions $M\left(\frac{1}{2} \pm \frac{\lambda-1/2}{\nu}, 1, \mp\nu v\right)$ and $U\left(\frac{1}{2} \pm \frac{\lambda-1/2}{\nu}, 1, \mp\nu v\right)$ (see Eqs. A.9, 10, 12, 13).

The function $\hat{f}(u)$ of interest in our problem satisfies $\hat{f}(D_\pm) = 0$. As $D_- < 0 < D_+$, we are led to introduce two functions $\hat{f}(u)$, one for positive u and one for negative u.

$$\begin{aligned} \hat{f}(u>0) &= a_+\mathcal{M}(1+u) + b_+\mathcal{U}(1+u) \\ \hat{f}(u<0) &= a_-\mathcal{M}(1-u) + b_-\mathcal{U}(1-u). \end{aligned} \quad (26)$$

The four coefficients $a_\pm$ and $b_\pm$ are determined by enforcing the boundary conditions $\hat{f}(D_\pm) = 0$ and by requiring that $\hat{f}$ and $\hat{f}'$ are continuous for $u = 0$, as the full wave function $\langle\,\mathbf{r}|\varphi\rangle$ close to the impurity has this property. The corresponding set of equations reads

$$\begin{aligned} & a_\pm\,\mathcal{M}(1\pm D_\pm) + b_\pm\,\mathcal{U}(1\pm D_\pm) = 0 \\ & a_+\,\mathcal{M}(1) + b_+\,\mathcal{U}(1) = a_-\,\mathcal{M}(1) + b_-\,\mathcal{U}(1) \\ & a_+\,\mathcal{M}'(1) + b_+\,\mathcal{U}'(1) = -a_-\,\mathcal{M}'(1) - b_-\,\mathcal{U}'(1). \end{aligned} \quad (27)$$

This set of homogeneous equations has a non zero solution only if its determinant is zero. This condition reads

$$(A_0 - A_-)\,(B_0 - A_+) + (A_0 - A_+)\,(B_0 - A_-) = 0 \quad (28)$$

with

$$A_\pm = \frac{\mathcal{M}(1\pm D_\pm)}{\mathcal{U}(1\pm D_\pm)} \quad A_0 = \frac{\mathcal{M}(1)}{\mathcal{U}(1)} \quad B_0 = \frac{\mathcal{M}'(1)}{\mathcal{U}'(1)}\cdot \quad (29)$$

From the corresponding $a_\pm$ and $b_\pm$, we get the function $\hat{f}(u)$ as

$$\hat{f}(u) = a(A_0 - A_\pm)[\mathcal{M}(1\pm u) - A_\pm\,\mathcal{U}(1\pm u)] \quad (30)$$

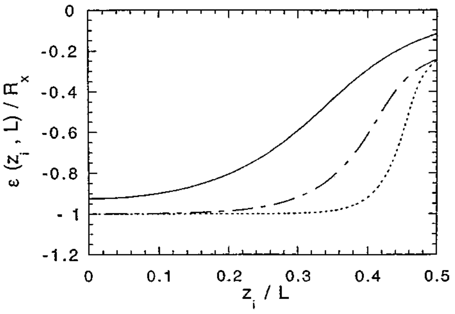


Fig. 1. Ground state energy in Rydberg unit as a function of the reduced impurity position z_i/L in a well of width L for $L/a_x = 20$ (dotted line), $L/a_x = 10$ (dashed line), $L/a_x = 5$ (solid line), a_x being the Bohr radius. The limiting values for large L are -1 for $z_i = 0$ and $-1/4$ for $z_i = L/2$.

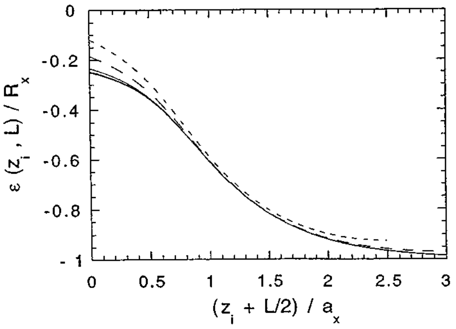


Fig. 2. Ground state energy in Rydberg unit as a function of the absolute impurity position in Bohr radius unit a_x, starting from the well border $-L/2$ for $L/a_x = 5$ (small dashed line), $L/a_x = 6$ (large dashed line). For $L/a_x \geq 8$ (solid lines) the curves are almost indistinguishable. The limiting values for large L are $-1/4$ for $z_i + L/2 = 0$ and -1 for $z_i = 0$.

where the upper sign corresponds to $u > 0$ and the lower one to $u < 0$, the prefactor a being determined from the normalization condition equation (8).

Equation (28) contains the parameters ν, λ, L and z_i. From it, we can numerically determine ν as a function of λ, L and z_i. By inserting this $\nu(\lambda, L, z_i)$ into equation (23), we determine the value of λ which minimizes $\langle \varphi|H|\varphi \rangle$; and from it, we finally obtain the ground state energy as a function of L and z_i, equation (30) giving the corresponding exact envelope function.

4 Discussions and results

Figure 1 shows this ground state energy $\varepsilon(z_i, L)$ as a function of the relative impurity position z_i/L for three rather large values of L/a_x, namely $L/a_x = 20, 10, 5$. As expected, we see that this energy essentially goes from $(-R_x)$ to $(-R_x/4)$ when the impurity moves from the center to the border of the well. We can also check that these curves move up when L decreases, due to the confinement. Except for quite narrow wells, this effect is however very small, even for intermediate L as can be seen on Figure 2 which shows the energies for various L/a_x, as a function of the absolute impurity position of z_i, starting from $z_i = -L/2$: we see that $\varepsilon(z_i, L)$ strongly decreases over a distance of the order of $2a_x$ from the well border, this decrease being essentially the same for all L larger than $8a_x$. Actually, $8a_x$ corresponds to a rather narrow quantum well if we note that all the points of such a $(8a_x)$ width well lie within less than $(4a_x)$ from the walls.

In Figure 3, we show the same energies $\varepsilon(z_i, L)$ as a function of L, in the large L range, for three positions of the impurity. The dashed curves correspond to these energies calculated with the free electron envelope function $f(z) = \cos(\pi z/L)$. We see that the exact $f(z)$ generates an energy typically 10% lower than the one obtained from this free electron $f(z)$, which is pretty sizeable and in any case much more than what we anticipated.

In Figure 4, we plot the logarithm of the difference between these $\varepsilon(z_i, L)$ and their large L asymptotic values. We do check that these asymptotic values are reached with exponentially small corrections once L is larger than $4a_x$. It is actually surprising to find an extremely straight Ln plot, which indicates that these corrections behave exponentially for wells as narrow as $4a_x$. We also see in Figure 4 that the free electron envelope function $f(z) = \cos(\pi z/L)$ gives larger corrections which are not exponentially small, in agreement with equation (15).

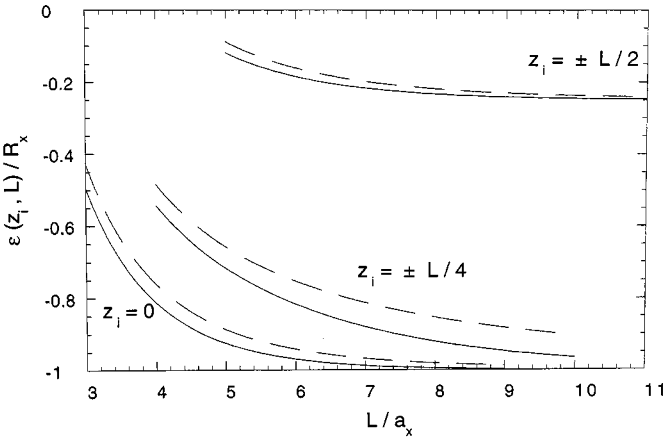


Fig. 3. Ground state energy in Rydberg unit as a function of the well width L in Bohr radius unit a_x, for three impurity positions: $z_i = 0$ (plotted for L/a_x going from 3 to 9), $z_i = \pm L/4$ (plotted for L/a_x going from 4 to 10) and $z_i = \pm L/2$ (plotted for L/a_x going from 5 to 11). The dashed lines correspond to the same energy calculated with $f(z) = \cos \pi z/L$.

The appropriate way to present the energy for fixed z_i as a function of L, starting from $L = 0$, is to plot the binding energy $\varepsilon_{\rm B}(z_i, L)$ defined in equation (4) as this quantity stays finite when $L \to 0$. Figure 5a shows this binding energy for all L and Figure 5b shows it for narrow wells only. As expected, when L increases from 0 to ∞, this binding energy increases from $(-4R_x)$ to $(-Rx)$ for $z_i = 0$ and from $(-4R_x)$ to $(-R_x/4)$ for $z_i = L/2$. Let us stress that these binding energies still vary significantly up to $L/a_x \approx 8$ due to the confinement energy introduced artificially in $\varepsilon_{\rm B}(L, z_i)$, while the large L asymptotic values are reached much faster for $\varepsilon(z_i, L)$. This $\varepsilon_{\rm B}$ is indeed

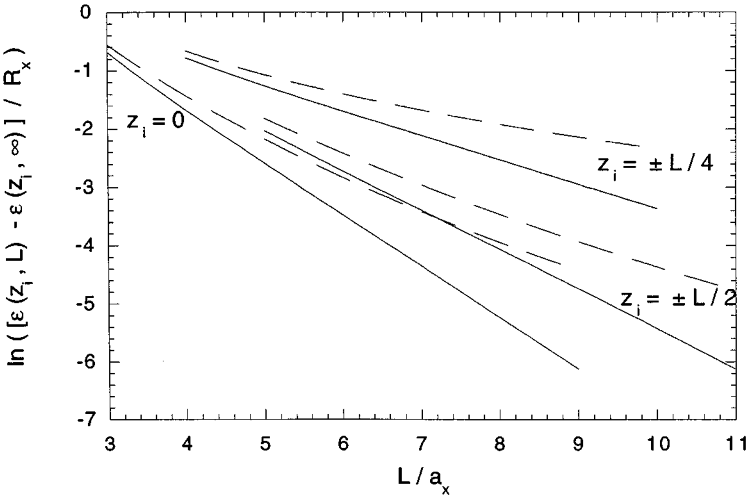
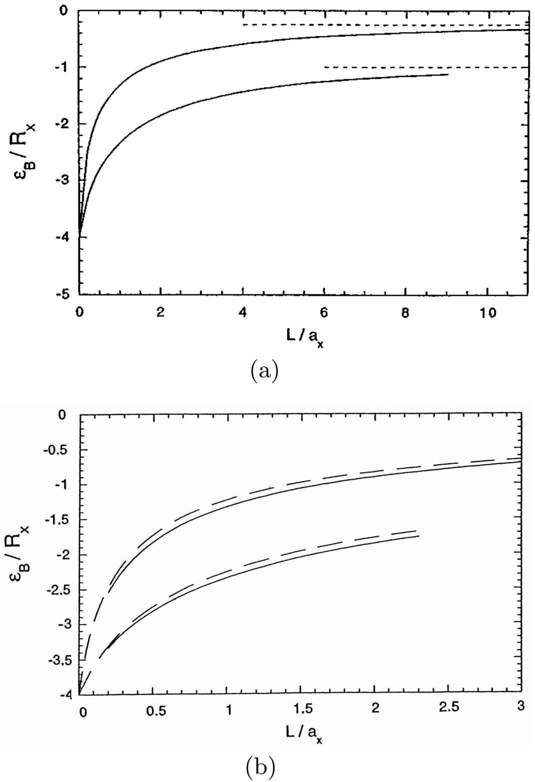


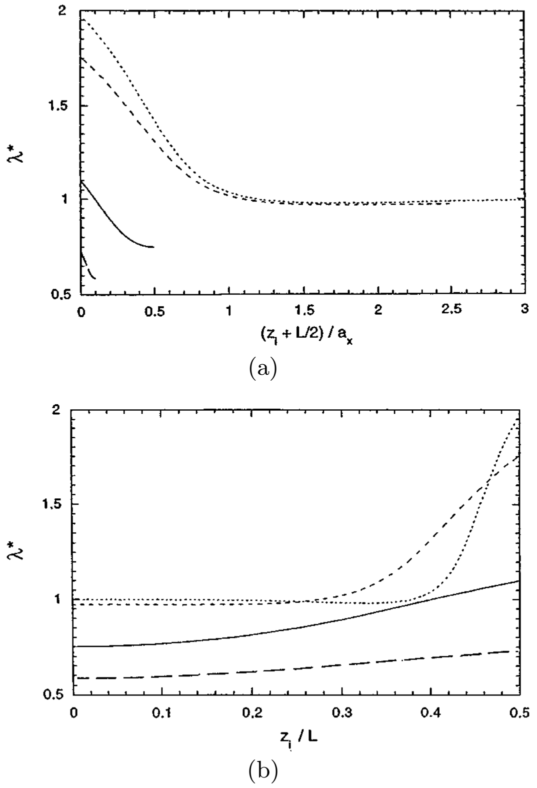
Fig. 4. Logarithm of the difference between the energy and its large L asymptotic value as a function of the well width L for three impurity positions when calculated with the exact $f(z)$ (solid lines): $z_i = 0$ (plotted for L/a_x going from 3 to 9), $z_i = \pm L/4$ (plotted for L/a_x going from 4 to 10) and $z_i = \pm L/2$ (plotted for L/a_x going from 5 to 11). A linear dependence indicates that the corrections to the asymptotic value behave exponentionally in L/a_x. At this scale the solid line is essentially indistinguishable from a straight line. The dashed lines correspond to the same energy calculated with $f(z) = \cos \pi z/L$.



(a)

(b)

Fig. 5. Upper panel: binding energy ε_{B} as a function of the well width L in Rydberg unit, for $z_i = L/2$ (upper curve) and $z_i = 0$ (lower curve). The large L asymptotic values are respectively $-1/4$ and -1, while for $L \to 0$, ε_{B} goes to -4 for all impurity positions. Lower panel: same binding energies in the small L range. The dashed curves correspond to the energies calculated with $f(z) = \cos \pi z/L$.



(a)

(b)

Fig. 6. The parameter λ^* corresponding to the minimum of $\langle\varphi|H|\varphi\rangle$ for $L/a_x = 10$, 5, 1 and 0.2 , as a function of the impurity position z_i in a_x unit (upper panel) or in L unit (lower panel). For $L \to \infty$, the limiting values are 1 for $z_i = 0$ and 2 for $z_i = L/2$ while for $L \to 0$ the limit is 1/2 for all z_i.

appropriate in the small L limit in order to have a finite quantity, but rather meaningless for large L. In this limit, the Coulomb potential confines the electron close to the impurity so efficiently that the well confinement does not play any role.

Figure 6 shows the parameter λ^* corresponding to the minimum of $\langle\,\varphi|H|\varphi\,\rangle$ as a function of the impurity position z_i in a_x unit (Fig. 6a) and in L unit (Fig. 6b) for

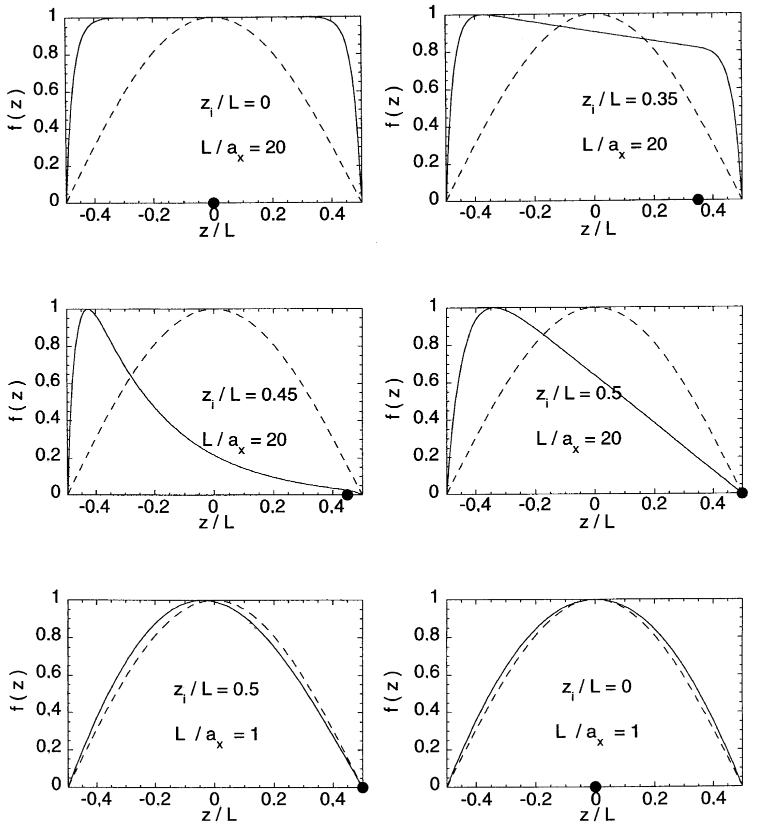


Fig. 7. The four upper graphs give the exact envelope function $f(z)$ as a function of z, in L unit, for $L/a_x = 20$ and various impurity positions z_i (indicated by the black dot). The two lower graphs give the same $f(z)$, but for $L/a_x = 1$. The dashed curves correspond to the usual free electron envelope function $f(z) = \cos \pi z/L$.

various well widths. This parameter essentially controls the extension of the wave function around the impurity. In the large L limit, λ^* is expected to vary from 1 to 2 when z_i goes from 0 to $\pm L/2$, while in the small L limit, λ^* goes to $1/2$ for all impurity positions. We see that, for large values of L, λ^* essentially increases over a distance a_x from the wall. We also see that for a given z_i, λ^* decreases when L decreases, in agreement with the predicted $\lambda^* = 1/2$ value for all z_i when $L \to 0$.

The last set of Figures 7 shows the exact $f(z)$ for various impurity positions and two well widths (a small one $L/a_x = 1$ and a large one $L/a_x = 20$). On the same figures is shown the usual free electron envelope function $f(z) = \cos(\pi z/L)$, which of course does not depend of the impurity position. We see that, for larger L, the exact $f(z)$ is quite different from the envelope function for all impurity positions, being much flatter than $\cos(\pi z/L)$ close to the impurity, *i.e.*, in the region which matters for calculating the energy. We also see that the usual envelope function is of course much better for narrow wells than for large ones, although the difference is still noticeable for width as small as a_x.

Conclusion

We have determined the ground state energy of an electron bound to an impurity located at $\mathbf{r}_i$ inside a quantum well, by using a variationnal procedure which relies on a trial wave function $f(z)\mathrm{e}^{-|\mathbf{r}-\mathbf{r}_i|/\lambda a_x}$ in which $f(z)$ is the *exact* function which gives the minimum ground state energy. We show that, for large wells, the exact envelope function $f(z)$ is *quite different* from the free electron envelope function $f(z) = \cos(\pi z/L)$ used up to now. Moreover, the energy obtained from this free electron $f(z)$ has spurious terms in $(a_x/L)^2$ which makes it unsuitable for the determination of the exciton dead layer in large width quantum wells we are going to present in a forthcoming paper. We have checked that our new method does produce corrective terms to these large L limits which are indeed exponentially small.

The energies we find from this new variationnal procedure are lower than the preceding ones by approximatively 10% for intermediate well widths, the previous variationnal approach [1] being designed to obtain the large L and small L limits correctly.

In the procedure presented here, we have considered a model quantum well with infinitely high barriers only. Although somewhat heavier, the same functional derivative method can be extended to finite barrier heights. We plan to present this extension in a forthcoming publication.

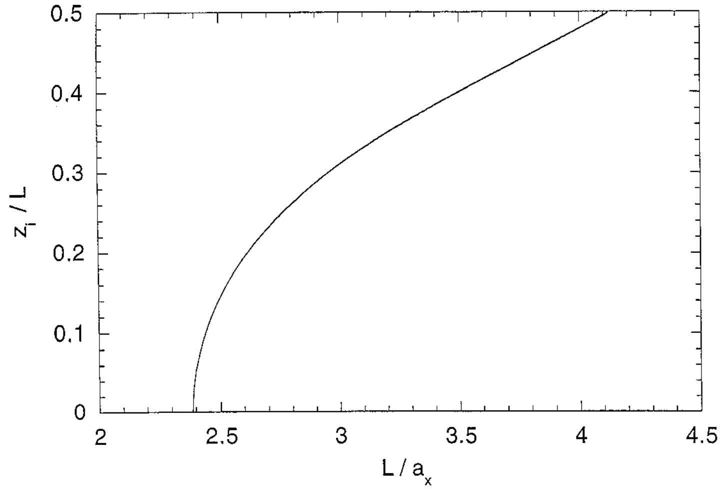


Fig. 8. Values of impurity position z_i as a function of well width L for which the energy $\varepsilon(z_i, L)$ is zero. We see that the energy is always positive for $L/a_x \leq 2.4$ and always negative $L/a_x \geq 4.1$.

Appendix: General solution of the differential equation (19)

Let us introduce the variable $v = 1 + |u|$ and set

$$\hat{f}(u) = \tilde{f}(v). \tag{A.1}$$

As $\mathrm{d}v/\mathrm{d}u = |u|/u$, the differential equation (19) satisfied by $\hat{f}$ reads in terms of $\tilde{f}$

$$4v\tilde{f}'' + 4(1-v)\tilde{f}' + [4(\lambda - 1) + (1-\nu^2)v]\tilde{f} = 0 \tag{A.2}$$

with $\nu^2 = 4\chi' - 1$. For large v, this differential equation reduces to

$$4\tilde{f}''_\infty - 4\tilde{f}'_\infty + (1-\nu^2)\tilde{f}_\infty = 0. \tag{A.3}$$

Its two solutions are $\exp(\beta_\pm v)$ with $\beta_\pm = (1 \pm \nu)/2$. If we extract this large v limit and set

$$\tilde{f}(v) = \mathrm{e}^{\beta v} k(v) \tag{A.4}$$

where β is one of the two $\beta_\pm$, equation (A.2) gives

$$vk'' + [1 + (2\beta - 1)v]k' + (\beta + \lambda - 1)k = 0 \tag{A.5}$$

i) for $2\beta - 1 \neq 0$, we can transform this equation into the differential equation for degenerate hypergeometric functions, namely

$$z\omega'' + (\gamma - z)\omega' - \alpha\omega = 0 \tag{A.6}$$

of which two independent solutions [11] are $M(\alpha, \gamma, z)$ and $U(\alpha, \gamma, z)$. Indeed by setting

$$k(v) = \omega(z) \tag{A.7}$$

with $z = (1 - 2\beta)v$, equation (A.5) gives

$$z\omega'' + (1 - z)\omega' + \frac{\beta + \lambda - 1}{1 - 2\beta}\omega = 0 \tag{A.8}$$

the solutions of which are the two degenerate hypergeometric functions corresponding to $\alpha = (1 - \beta - \lambda)/(1 - 2\beta)$ and $\gamma = 1$.

As we can *a priori* take either $\beta = \beta_+$ or β_- (*i.e.* $2\beta - 1 = \pm\nu$), this procedure generates four possible solutions for the second order differential equation (A.2), namely

$$M_\pm(v) = \mathrm{e}^{(1\pm\nu)v/2}\, M\left(\frac{1}{2} \pm \frac{\lambda - 1/2}{\nu}, 1, \mp\nu v\right) \tag{A.9}$$

$$U_\pm(v) = \mathrm{e}^{(1\pm\nu)v/2}\, U\left(\frac{1}{2} \pm \frac{\lambda - 1/2}{\nu}, 1, \mp\nu v\right) \tag{A.10}$$

whereas we only need two independent solutions. We first note that the two $M_\pm(v)$ are in fact identical due to

$$M(\alpha, \gamma, z) = \mathrm{e}^z\, M(\gamma - \alpha, \gamma, -z). \tag{A.11}$$

On the opposite, the two $U_\pm(v)$ are different as a similar relation does not exist for $U(\alpha, \gamma, z)$. We can however check that $M_\mp(v)$, $U_+(v)$ and $U_-(v)$ are indeed linearly dependent due to relations between the $M(\alpha, \gamma, z)$ and the $U(\alpha, \gamma, z)$.

As for imaginary ν, $U_+(v)$ and $U_-(v)$ are complex conjugate, we choose the two independent solutions of equation (A.2) as

$$\mathcal{M}(v) = M_+(v) = M_-(v) \tag{A.12}$$

$$\mathcal{U}(v) = \frac{1}{2}[U_+(v) + U_-(v)] \tag{A.13}$$

since these two functions are real for all real or imaginary ν.

ii) For $\beta = 1/2$ *i.e.* $\nu = 0$, the above procedure fails, (as obvious from the pathology of $M_\pm(v)$ and $U_\pm(v)$ when $\nu \to 0$). In this case, it is possible to transform equation (A.5), into the differential equation for Bessel functions. The two independent solutions for $k(v)$ are then $J_0(2[(\lambda - 1/2)v]^{1/2})$ and $Y_0(2[(\lambda - 1/2)v]^{1/2})$ which are real for the λ of interest, namely $\lambda > 1/2$. When $\nu = 0$, the energy $\varepsilon(z_i, L)$ is zero. Figure 8 shows the set of (z_i, L) which corresponds to $\varepsilon(z_i, L) = 0$: For $L/a_x > 4.1$ the energy is negative for all impurity positions, while for $L/a_x < 2.4$, it is always positive, due to confinement. Our numerical calculations for $\nu \neq 0$ are in very good agreement with this independent calculation for this specific case.

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