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# Ground-state energy of a $D^-$ ion in two-dimensional semiconductors

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The ground-state energy of a $D^-$ ion (a donor impurity ion with two attached electrons) in a two-dimensional semiconductor is calculated using a variational approach and is found to be about $-4.48$ Ry. The ground-state energy of a hydrogenic system in two dimensions is known to be $-4$ Ry. Thus the binding energy of a $D^-$ ion, defined as the energy required to remove one of the two electrons from the $D^-$ ion to infinity, is about 0.48 Ry. This is about 12% of the ground-state energy of a hydrogenic system in two dimensions. This is to be compared with the binding energy of a $D^-$ ion in three dimensions which is 5.55% of the hydrogenic ground-state energy. The relevance of our results to the problem of a $D^-$ ion in thin-quantum-well structures is discussed.

## I. INTRODUCTION

The study of the electronic structure of a negative hydrogen ion, namely a hydrogen atom with an extra electron attached to it, has attracted considerable attention since the early days of quantum mechanics.[1,2] The best variational calculation gives 1.0555 Ry (Ref. 2) for the ground-state energy of this system. In addition, it has recently been shown[3] that the system has one and only one bound state.

It was Lampert[4] who first suggested that it should be possible for an analogous system, namely, a donor impurity ion with two attached electrons, referred to as a $D^-$ ion, to exist in semiconductors. The binding energy of the $D^-$ ion, defined as the energy required to remove one of the two electrons from the $D^-$ ion to infinity, is rather small in most semiconductors. Thus conclusive evidence concerning the existence of this system in semiconductors was not available until recently. In the past few years, however, considerable information concerning the behavior of $D^-$ centers in semiconductors, especially Si and Ge, has become available.[5] The effects of magnetic[6] and stress[7] fields and of electron-phonon[8] interaction on the properties of $D^-$ ions have also been investigated both theoretically[6–8] and experimentally.[5] Recently, we have calculated[9] the effect of screening due to the presence of other free carriers on the binding energy of a $D^-$ ion.

Though considerable effort has been devoted toward understanding the behavior of $D^-$ centers in bulk semiconductors in the past several years, very little information seems to be available concerning the properties of $D^-$ ions in two-dimensional systems. The study of the properties of systems in two dimensions has a basic interest in its own right, as reducing the dimensionality often introduces novel and interesting features.[10] Our interest in the study of the $D^-$ ion in two dimensions is also motivated by the following reasons. With the recent advances in the epitaxial crystal growth techniques such as molecular beam epitaxy and metal-organic chemical vapor deposition, it has become possible to grow systems consisting of alternate layers of two different semiconductors with controlled thicknesses. Such systems are generally referred to as superlattices. One of the most thoroughly studied superlattices is the one consisting of alternate layers of GaAs and GaAlAs with layer thicknesses varying from about 20–400 Å. Depending on the Al concentration in GaAlAs, its band gap can be made considerably larger than that of GaAs. This leads to discontinuities at the conduction- and valence-band edges at the interfaces, thus confining electrons and holes in the GaAs quantum wells. The study of the properties of physical systems in these quantum-well structures has become of considerable interest in the past few years. For instance, Bastard[11] has recently calculated the binding energy of a donor in a GaAs quantum well as a function of the thickness of the well assuming infinite potential barriers at the interfaces. In order to check the reliability of the wave function used to calculate the energy levels one needs to know the behavior of a donor in the limiting cases of zero thickness (two dimensions) and infinite thickness (three dimensions). This provides an additional incentive for the study of systems in two dimensions. Actually, the potential barriers at the interfaces are finite. Mailhout *et al.*[12] and Greene and Bajaj[13] have calculated the energy levels of a hydrogenic donor in quantum-well structures using finite values of the potential offsets at the interfaces. It is, however, still of interest to study systems in two dimensions to provide guidance to calculations done with finite potential barriers. In addition, the study of two-dimensional systems is of considerable relevance in layered semiconductors.

In this paper we report a first calculation of the ground-state energy of a $D^-$ ion in a two-dimensional semiconducting system using a variational approach. We find that the value of the ground-state energy is $-4.48$ Ry where Ry is the hydrogenic Rydberg in three dimensions. The value of the binding energy of a hydrogenic system in two dimensions is known to be 4 Ry.[10] Thus the binding energy of a $D^-$ ion in two dimensions is about 0.48 Ry, which is 12% of the binding energy of a hydrogenic system in two dimensions. This is to be compared with the binding energy of a $D^-$ ion in three dimensions, which is 5.55% of the hydrogenic binding energy.

## II. THEORY

The Hamiltonian of our system consisting of two conduction electrons, each with an effective mass $m$, bound to the positive ion of an impurity atom in a two-dimensional semiconductor can be written as

$$H=\frac{p_1^2}{2m}+\frac{p_2^2}{2m}-\frac{e^2}{\epsilon_0 r_1}-\frac{e^2}{\epsilon_0 r_2}+\frac{e^2}{\epsilon_0 r_{12}}, \tag{1}$$

where $\vec{p}_1$ and $\vec{p}_2$ are the momentum operators of electrons 1 and 2, respectively, $\vec{r}_1$ and $\vec{r}_2$ designate the positions of electrons 1 and 2 from the positive ion assumed to be localized at the origin, and $\epsilon_0$ is the dielectric constant of the material. We have assumed that the conduction band is simple and isotropic and that the effective-mass approximation is valid. The distances $r_1$, $r_2$, and $r_{12}$ in two dimensions are defined as

$$r_1=(x_1^2+y_1^2)^{1/2},\quad r_2=(x_2^2+y_2^2)^{1/2},$$

and (2)

$$r_{12}=|\vec{r}_1-\vec{r}_2|\,.$$

Now, expressing all distances in terms of Bohr radius $a$ and all energies in terms of an impurity Rydberg $R$ for a three-dimensional system, namely

$$a=\frac{\epsilon_0\hbar^2}{me^2}\ \text{and}\ R=\frac{e^2}{2\epsilon_0 a}, \tag{3}$$

the Hamiltonian of a $D^-$ center can be written as

$$H=-(\nabla_1^2+\nabla_2^2)-\frac{2}{r_1}-\frac{2}{r_2}+\frac{2}{r_{12}}. \tag{4}$$

Here, of course, we have assumed that the values of the effective mass and the dielectric constant are the same in two- and three-dimensional semiconducting systems.

Exact analytic solutions of the Schrödinger equation for this Hamiltonian are not known. We shall therefore follow a variational approach to calculate its ground-state energy. The properties of a $D^-$ ion in three dimensions have been studied in great detail in recent years.[9] Several different trial wave functions have been used to calculate its ground-state energy. Recently, we have found[9] that the following form of the trial wave function,

$$\psi=\exp[-\lambda(r_1+r_2)]\sum_{L,M,N} C_{LMN}r_{12}^L r_1^M r_2^N, \tag{5}$$

leads to a very good value of the ground-state energy of a $D^-$ ion in three dimensions. Here $\lambda$ is a nonlinear variational parameter, $L$, $M$, and $N$ are positive integers including zero, and $C_{LMN}$ are coefficients to be determined by minimizing the ground-state energy: for instance, summing over all the positive integers $L$, $M$, and $N$ such that

$$0\le L+M+N\le 4 \tag{6}$$

leads to 35 terms in the expansion of this wave function. With this particular choice of the wave function, the ground-state energy of a $D^-$ ion in three dimensions is found[9] to be $-1.0553$ Ry, which is very close to the very accurate value of $-1.0555$ Ry.[2] We shall therefore use this form of the trial wave function to calculate the ground-state energy of a $D^-$ ion in two dimensions.

We minimize the following expressions for energy:

$$E=\frac{\int\psi^*H\psi}{\int\psi^*\psi}d\tau\,, \tag{7}$$

where $d\tau=d\vec{r}_1 d\vec{r}_2$. The resultant integrals are of the form

$$I(p_1,p_2,p_3)=\int r_{12}^{p_1-1}r_1^{p_2-1}r_2^{p_3-1}\times\exp[-2\lambda(r_1+r_2)]d\tau\,, \tag{8a}$$

where $p_1$, $p_2$, and $p_3$ are positive integers including zero, the volume element

$$d\tau=\frac{4\pi r_1 r_2 r_{12}dr_1 dr_2 dr_{12}}{[(r_1+r_2+r_{12})(r_1+r_2-r_{12})(r_1-r_2+r_{12})(-r_1+r_2+r_{12})]^{1/2}}\,, \tag{8b}$$

and the limits of integration are $r_1 \geq 0$, $r_2 \geq 0$, and $|r_1 - r_2| \leq r_{12} \leq |r_1 + r_2|$. The evaluation of the integrals of the form $I(p_1,p_2,p_3)$ is briefly outlined in the Appendix.

## III. RESULTS AND DISCUSSION

We have calculated the ground-state energy ($E$) of a $D^-$ ion in two dimensions using several different sets of terms in the expansion of the wave function $\psi$. For instance, for

$$L + M + N \leq k$$

the calculation for $k=1$ leads to four terms in the expansion and yields $-4.3438$ for the ground-state energy. For $k=2$ (10 terms) the calculation gives $-4.4751$, for $k=3$ (17 terms) gives $-4.4776$, and for $k=4$ (35 terms) it leads to $-4.4801$. The difference in $E$ for $k=3$ and 4 is quite small and thus the use of $k=5$ is not expected to improve the results significantly. It is interesting to compare these values with those of a $D^-$ ion in three dimensions using the same form of the trial wave function. In this case we find that the ground-state energy is $-1.019$ for $k=1$, $-1.053\,18$ for $k=2$, $-1.053\,76$ for $k=3$, and $-1.055\,34$ for $k=4$. The relative difference between values of $E$ for $k=3$ and 4 in two dimensions is much smaller than that in three dimensions, though the absolute differences are comparable. Thus the relative rate of convergence is considerably better in two dimensions. As mentioned earlier, a very accurate value of $E$ in three dimensions is found to be $-1.0555$, which is very close to our value for $k=4$. We therefore believe that the value of $E$ in two dimensions (2D) that we calculate for $k=4$ should be very close to the "exact" value. The binding energy ($E_B$) of a $D^-$ ion, defined as the energy required to remove one of the two electrons from the $D^-$ ion to infinity, is defined as

$$E_B = -E - E_{2\mathrm{D}} , \tag{9}$$

where $E_{2\mathrm{D}}$ is the donor binding energy in two dimensions. The value of $E_{2\mathrm{D}}$ is known to be 4.[10] Thus the value of $E_B$ in two dimensions is about 0.48, which is 12% of $E_{2\mathrm{D}}$. This is to be compared with the value of $E_B$ in three dimensions, which is about 5.55% of $R$. Thus in two dimensions the second electron in a $D^-$ ion is proportionately more bound than in three dimensions: almost by a factor of 2. This is to be expected, as reducing the dimensionality often leads to more binding. What is new and interesting about this result is the magnitude of the binding energy ($E_B$) in two dimensions.

As pointed out earlier, the study of the $D^-$ ion in two dimensions is of considerable relevance to the GaAs-$\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ quantum-well structures. For GaAs quantum-well sizes less than 100 Å, the binding energy of a $D^-$ ion is expected to be significantly larger than its value in bulk GaAs, thus making its experimental observation somewhat easier. A study of the variation of the binding energy of a $D^-$ ion as a function of the GaAs quantum-well size is planned for future publication.

It is well known that the $D^-$ ion has one and only one bound state in three-dimensional systems.[2] A *zero*-orbital angular momentum triplet state of a $D^-$ ion in two dimensions can be easily constructed within the framework of our trial wave function by antisymmetrizing it relative to the interchange of electron spatial coordinates. Using this wave function we have calculated the energy of this state and find that it is not bound. It should be interesting to determine whether higher angular momentum triplet states are bound. Such a study is planned for future publication.

## APPENDIX: EVALUATION OF $I(p_1,p_2,p_3)$

The calculation of the integrals of the type $I(p_1,p_2,p_3)$ is greatly facilitated by using the following coordinate transformation. Define

$$s = r_1 + r_2 - r_{12} , \tag{A1}$$

$$t = r_1 - r_2 + r_{12} , \tag{A2}$$

$$u = -r_1 + r_2 + r_{12} . \tag{A3}$$

Thus

$$d\tau = \pi\sqrt{2}\,\frac{r_1 r_2 r_{12}\, ds\, dt\, du}{[stu\,(s+t+u)]^{1/2}} , \tag{A4}$$

where the limits of integration for $s$, $t$, and $u$ are from 0 to $\infty$. Integral $I(p_1,p_2,p_3)$ then takes the following form:

$$I(p_1,p_2,p_3) = \pi\sqrt{2}\int_0^\infty ds \int_0^\infty dt \int_0^\infty \frac{du\,[\tfrac{1}{2}(t+u)]^{p_1}[\tfrac{1}{2}(s+t)]^{p_2}[\tfrac{1}{2}(u+s)]^{p_3}}{[stu\,(s+t+u)]^{1/2}} \exp[-\lambda(t+u+2s)] , \tag{A5}$$

which is easily expressed as a linear combination of integrals of the form

$$J(a,b,c)=\int_0^\infty ds\int_0^\infty dt\int_0^\infty du\,\frac{s^{a-1/2}t^{b-1/2}u^{c-1/2}\exp[-(t+u+2s)]}{(s+t+u)^{1/2}} \tag{A6}$$

$$=\Gamma(a+\tfrac{1}{2})\Gamma(b+\tfrac{1}{2})\Gamma(c+\tfrac{1}{2})\int_0^\infty \frac{dp}{\sqrt{p}\,(2+p)^{a+1/2}(1+p)^{b+1/2}(1+p)^{c+1/2}}\ , \tag{A7}$$

where $\Gamma(x)$ is a $\Gamma$ function, after scaling $s$, $t$, and $u$ by $\lambda$, and using results of Ref. 14. Integral $J$ can be further reduced to integrals of the form

$$g_{\alpha,\beta}=\int_0^1\frac{(1-y)^\alpha dy}{(2-y)^{\beta+1/2}\sqrt{y}} \tag{A8}$$

by letting

$$y=\frac{p}{1+p}\quad\text{and } \alpha=a+b+c \tag{A9}$$

in Eq. (A7). These integrals are easily evaluated recursively, using

$$g_{0,0}=\pi/2\ , \tag{A10}$$

$$g_{0,\beta+1}=(\tfrac{1}{2}+\beta g_{0,\beta})/(2\beta+1)\quad\text{for } \beta>0 \tag{A11}$$

$$g_{0,-|\beta|}=[\tfrac{1}{2}+(2|\beta|-1)g_{0,-|\beta|+1}]/|\beta|\quad\text{for } \beta<0 \tag{A12}$$

and

$$g_{\alpha,\beta}=g_{\alpha-1,\beta-1}-g_{\alpha-1,\beta}\ , \tag{A13}$$

where $\alpha$ and $\beta$ are integers.

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[1] H. A. Bethe and E. E. Salpeter, in *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957), p. 154.

[2] C. L. Perkeris, Phys. Rev. 112, 1649 (1958); 126, 1470 (1962).

[3] R. N. Hill, Phys. Rev. Lett. 38, 643 (1977).

[4] M. A. Lampert, Phys. Rev. Lett. 1, 450 (1958).

[5] For a review of this work, see S. Narita, J. Phys. Soc. Jpn. 49, Suppl. A, 173 (1980), and references cited therein.

[6] David M. Larsen, Phys. Rev. B 20, 5217 (1979); 23, 4076 (1981).

[7] David M. Larsen, Phys. Rev. B 23, 5521 (1981).

[8] David M. Larsen, Phys. Rev. B 23, 628 (1981).

[9] Dwight E. Phelps and K. K. Bajaj, Phys. Rev. B 26, 912 (1982).

[10] For an excellent recent review on the properties of two-dimensional systems, see T. Ando, A. B. Fowler, and Frank Stern, Rev. Mod. Phys. 54, 437 (1982).

[11] G. Bastard, Phys. Rev. B 24, 4714 (1981).

[12] C. Mailhout, Y. C. Chang, and T. C. McGill, Phys. Rev. B 26, 4449 (1982).

[13] R. L. Greene and K. K. Bajaj, Solid State Commun. (in press).

[14] I. S. Gradshteyn and I. M. Ryzhik, in *Tables of Integrals, Series, and Products* (Academic, New York, 1965), p. 622.