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Eigenstates of Wannier excitons near a semiconductor surface

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The exact energies and wave functions, in the effective-mass approximation, of an electron moving in the potential of a massive hole near a single rigid surface of a semiconductor are presented. The electron-hole interaction potential is taken to be the Coulombic $1/\epsilon r$ inside the semiconductor and $+\infty$ outside. The Schrödinger equation for this electron-hole interaction potential is separable in the prolate spheroidal coordinate system, and thus can be solved numerically to any desired accuracy rather easily. The ground state of the exciton is seen to change continously from a hydrogenic $1s$ state, when the hole is well inside the bulk, to a hydrogenic $2p_z$ state, when the hole is located right on the surface in agreement with the known results in these two limits. The variation of the energies and wave functions of the ground and the excited states as a function of the distance of the hole from the surface are discussed and compared with some previous calculations.

I. INTRODUCTION

A hydrogenic model describes very well the eigenstates of excitons in the bulk of a semiconductor.[1] An extension of this model to the case of excitons near crystalline surfaces would be useful in the understanding of many phenomena in surface semiconductor physics, e.g., the formation of a "dead layer,"[2,3] surface-reflectance spectra, etc. Numerous works, both theoretical[2–20] and experimental,[21,22] have dealt with the behavior of hydrogenic excitons in confined geometries. However, the finite mass of the electron and of the hole along with the presence of the crystalline boundary makes only approximate calculations possible.

In many of these theoretical works, therefore, attention has been focused on the simpler problem of the surface exciton with an infinitely heavy hole. Levine[8] noted that the eigenstates of an electron moving in the Coulombic potential of the immobile hole located right on the surface are simply those hydrogenic wave functions that vanish on the crystalline surface. Harper and Hilder,[4] and, more recently, Gallardo and Mattis,[7] have used an approximate Green's-theorem method to study the energy of the exciton at a finite distance from the wall. Bendow[6] has studied the effect of the finite geometry on the energy of an exciton by a variational calculation. However, such methods, as might be expected, yield poor results when the exciton is close to the wall.

Seemingly, it has not been realized that the eigenstates of an exciton with a massive hole ($m_e/m_h \rightarrow 0$) at a finite distance from a single semiconductor surface is exactly solvable. The aim of this paper is to provide such solutions. The same eigenstates also appear for an electron moving in the potential of a donor atom near a surface. The fact that this is one of the very few problems for which the Schrödinger equation is exactly soluble makes it interesting by itself.

II. THE HAMILTONIAN AND ITS SOLUTION

In the effective-mass approximation, the Hamiltonian of the exciton near a semiconductor surface is given by

$$H=-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_h}\nabla_h^2+V_{e\text{-}h}+V_s\ , \tag{1}$$

where m_e and m_h are, respectively, the effective masses of the electron and the hole. Here $V_{e\text{-}h}$ is the Coulombic electron-hole interaction potential

$$V_{e\text{-}h}=-1/\epsilon\,|\vec{r}_e-\vec{r}_h|\ , \tag{2}$$

ϵ being the dielectric constant of the medium, and $\vec{r}_e$ and $\vec{r}_h$ are, respectively, the positions of the electron and the hole. V_s is the potential due to the surface located at $z=a$, and it includes the image potential. We shall restrict ourselves to the case of the heavy holes such that the hole motion may be completely neglected. We shall also neglect the image potential and assume the customary boundary condition,[6–8,15,16] that the wave function vanishes on the surface. Neglect of the image potential while choosing the above boundary condition (BC) is justified,[13,15] since the repulsive image potential basically serves to decrease the amplitude of the wave function at the boundary. With these approximations, the Hamiltonian of Eq. (1) reduces to a simple hydrogenic Hamiltonian,

$$H=-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{1}{\epsilon\,|\vec{r}_e-\vec{r}_h|}\ , \tag{3}$$

with the BC

$$\psi(z_e=a)=0\ . \tag{4}$$

Here $z=a$ is the bounding plane of the crystal and z_e is the z coordinate of the electron.

The boundary condition given by Eq. (4) makes it difficult to solve the Schrödinger equation

$$H\psi=E\psi \tag{5}$$

of the surface exciton in the spherical coordinate system. However, as we shall soon see, the Schrödinger equation becomes separable in the prolate spheroidal coordinate system[23] making the exact solution easily obtainable. We define the new set of coordinates (ξ,η,ϕ) with

$$\xi=\frac{r_1+r_2}{2a}\,,\quad \eta=\frac{r_2-r_1}{2a}\,,$$

and ϕ is the rotational angle about the line passing through the hole and perpendicular to the surface. Here, r_1 is the distance between the electron and the hole, r_2 is the distance between the electron and the image of the hole, and a is the distance of the hole from the surface (see Fig. 1). This coordinate system is rather well known in connection with the hydrogen molecular ion.[24–28] In these coordinates the half-space geometry of the crystal is defined by ξ varying from 1 to ∞, η varying from 0 to 1, and ϕ varying from 0 to 2π. The boundary condition of Eq. (4) simply becomes

$$\psi(\eta=0)=0\ . \tag{6}$$

The Schrödinger equation given by Eqs. (3) and (5) in the prolate spheroidal coordinate system becomes

$$-\frac{1}{\xi^2-\eta^2}\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial\psi}{\partial\xi}+\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial\psi}{\partial\eta}+\frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2\psi}{\partial\phi^2}\right]-\frac{2a\psi}{\xi-\eta}=Ea^2\psi\ . \tag{7}$$

Here the energy unit is the Rydberg divided by ϵ^2 and the distance unit is the Bohr radius multiplied by ϵ, where ϵ is the dielectric constant of the medium. Writing

$$\psi(\xi,\eta,\phi)=\Phi(\phi)X(\xi)Y(\eta) \tag{8}$$

and substituting this expression in Eq. (7), the following three separated equations are obtained:

$$\frac{d^2\Phi}{d\phi^2}=-m^2\Phi\ , \tag{9}$$

$$\frac{d}{d\xi}(\xi^2-1)\frac{dX}{d\xi}-\left[\frac{m^2}{\xi^2-1}-2a\xi+k^2\xi^2+A\right]X=0\ , \tag{10}$$

and

$$\frac{d}{d\eta}(\eta^2-1)\frac{dY}{d\eta}-\left[\frac{m^2}{\eta^2-1}+2a\eta+k^2\eta^2+A\right]Y=0\ . \tag{11}$$

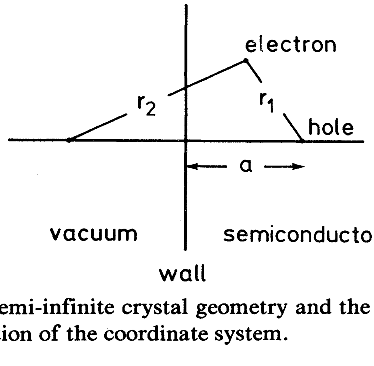

FIG. 1. Semi-infinite crystal geometry and the distances used in the definition of the coordinate system.

The boundary conditions are

$$\Phi(\phi=0)=\Phi(\phi=2\pi)\ , \tag{12}$$

$$X(\xi\to\infty)\to 0\ , \tag{13}$$

and

$$Y(\eta=0)=0\ . \tag{14}$$

In Eqs. (9)–(11), m and A are the separation constants and $k^2=-4a^2E$. We shall deal only with the bound-exciton states, so that k^2 is a positive quantity. The solutions of the ϕ equation (9), along with the BC, Eq. (12), are given by[29]

$$\Phi=\frac{1}{\sqrt{(2\pi)}}e^{\pm im\phi}\ , \tag{15}$$

where $m=0,1,2,3,\ldots$ is the azimuthal quantum number.

The ξ equation (10), along with the BC, Eq. (13), also arises in connection with the hydrogen molecular ion and has been studied by many authors.[24–28] Following Jaffè,[25] we write

$$X(\xi)=(\xi^2-1)^{m/2}(\xi+1)^{\sigma}e^{-k\xi}\sum_{n=0}^{\infty}a_n\left[\frac{\xi-1}{\xi+1}\right]^n\ , \tag{16}$$

with $\sigma=(2a/k)-(m+1)$. The advantage of expanding $X(\xi)$ in a power series of $(\xi-1)/(\xi+1)$ is that this series is rapidly convergent. Inserting Eq. (16) in the ξ equation (10), the following three-term recursion relations for the a_n's are obtained:

$$a_{n+1}=p_na_n+q_na_{n-1} \tag{17}$$

for $n\geq 0$, with $a_{-1}=0$. Here

$$p_n=\frac{A+k^2-2k\sigma-(\sigma+m)(m+1)-2n(\sigma-2k)+2n^2}{(n+1)(n+m+1)} \tag{18}$$

and

$$q_n=\frac{(n-1-\sigma)(m+\sigma+1-n)}{(n+1)(n+m+1)}\ . \tag{19}$$

The eigenvalues of the Schrödinger equation satisfy an equation, involving an infinite continued fraction, obtained from Eq. (17),

$$\frac{1}{p_0}=\frac{-p_1}{q_1}+\cfrac{\frac{1}{q_1}}{\frac{-p_2}{q_2}+\cfrac{\frac{1}{q_2}}{\frac{-p_3}{q_3}+\cfrac{\frac{1}{q_3}}{\frac{-p_4}{q_4}+\cdots}}}\ . \tag{20}$$

Here, p_i's and q_i's given by Eqs. (18) and (19) are functions of m, E, and A. Given the azimuthal quantum number m and a trial energy E, a separation constant A that satisfies Eq. (20) gives a solution of the ξ equation (10). An appropriate separation constant A may be found for every trial energy E. A solution is obtained if this A also satisfies the boundary condition of the η equation for the same trial energy E as discussed below.

The η equation (11), may be solved by writing

$$Y(\eta)=(\eta^2-1)^{m/2}e^{-k(\eta-1)}\sum_{n=0}^{\infty} b_n(\eta-1)^n \,. \tag{21}$$

Substitution of this expression for $Y(\eta)$ in Eq. (11) leads to a three-term recursion relation given by

$$b_{n+1}=r_n b_n+s_n b_{n-1}\,, \tag{22}$$

for $n\geq 0$, and with $b_{-1}=0$. We have here

$$r_n=\frac{A+k^2+(a/2)-(m-2k)(m+1)-2n(1-2k+m)-n(n-1)}{2(n+1)(n+m+1)} \tag{23}$$

and

$$s_n=\frac{(a/2)+2k(m+n)}{2(n+1)(n+m+1)}\,. \tag{24}$$

By inspection of Eq. (21), the BC on $H(\eta)$, given by Eq. (14), simply becomes

$$b_0-b_1+b_2-b_3+\cdots=0\,. \tag{25}$$

Thus a solution is obtained when the set of numbers (m,E,A) that satisfies Eq. (20) is also a solution of Eq. (25). These values of the eigenenergies and the corresponding separation constants E and A specify the exact solutions and are obtained by a systematic search of the simultaneous solutions of Eqs. (20) and (25) for a given azimuthal quantum number m. In actual calculations the infinite series appearing in Eqs. (16) and (21) are terminated once the solution (energy E and separation constant A) has converged to the desired accuracy.

III. GROUND STATE

The exact eigenstates of the surface exciton are known in two limits: when the exciton is far away from the surface[1] and when the hole is located right on the surface.[8] The first case is of course the case of a bulk exciton, where the ground state is a hydrogenic 1s state with the energy $E=-1\,\mathscr{R}^{\text{eff}}$ (the effective Rydberg). The exact solution in the latter case was, as already mentioned, pointed out by Levine.[8] The ground-state wave function in this case is simply a hydrogenic $2p_z$ state with the wave function vanishing on the wall and with the eigenenergy $E=-\frac{1}{4}\mathscr{R}^{\text{eff}}$. In Fig. 2 we have displayed the calculated energies of the ground state and the first two excited states as a function of the distance of the hole from the surface. The two known limits are reproduced and the energies monotonically decrease as the hole is moved away from the wall.

The wave functions are obtained from the expressions of Eqs. (8), (16), and (21). Figure 3 shows contours of the ground-state wave functions for five different values of hole distances from the wall. This shows how the ground state gradually changes from the hydrogenic 1s state to the $2p_z$ state as the hole approaches the wall. In Fig. 4 we have displayed the variation of the expectation value $\langle z_e\rangle$ of the electron with the hole position. At hole distances of a few effective Bohr radii the electronic charge cloud is centered more or less around the hole, and thus $\langle z_e\rangle$ approximately equals the distance of the hole from the wall. As the hole is brought closer to the wall, the electron follows the hole. However, there is a minimum distance of approach of the electron to the wall. Once this minimum approach is achieved, moving the hole any closer to the wall moves the electron away from it as the repulsive effect of the wall is strongly felt by the electron (Fig. 4).

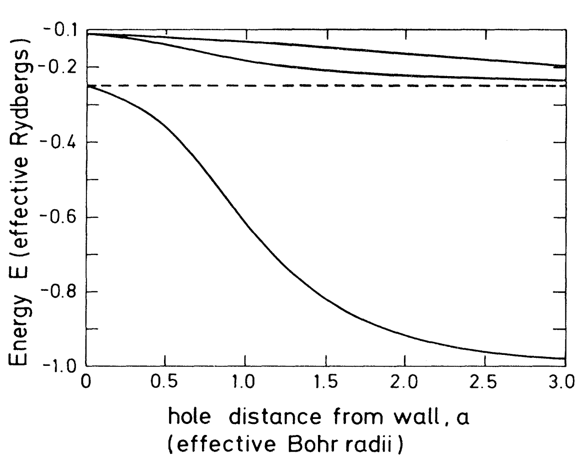

FIG. 2. Energies of the ground state and of the first two excited states as a function of the hole distance a from the wall.

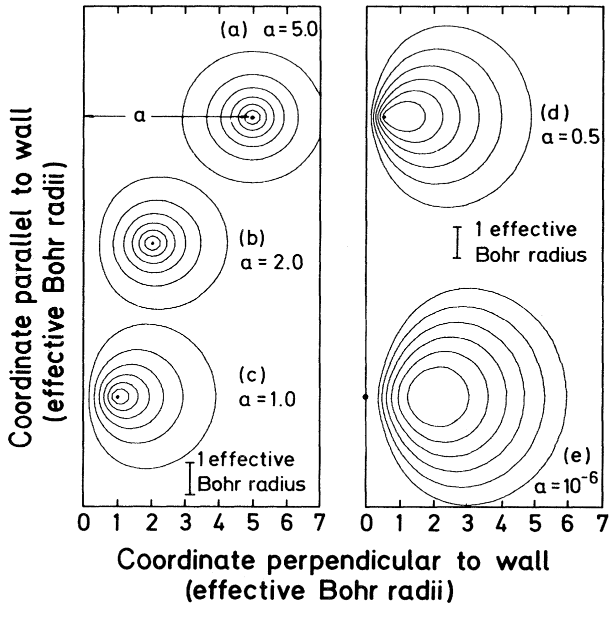

FIG. 3. Ground-state wave-function contours as the hole approaches the surface for various hole distances a: (a) $a=5$, (b) $a=2$, (c) $a=1$, (d) $a=0.5$, and (e) $a=10^{-6}$. Distances are in units of a_0.

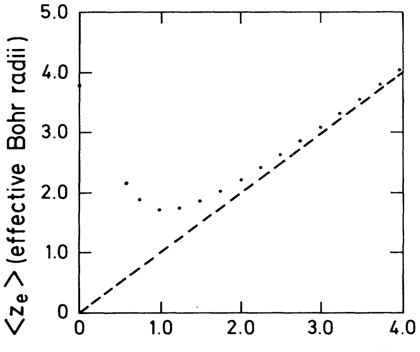

FIG. 4. Ground-state expectation value $\langle z_e \rangle$ of the distance of the electron from the wall as a function of the hole distance. Dashed line is the asymptote on which hole distance equals $\langle z_e \rangle$. Thus deviation of $\langle z_e \rangle$ from this line shows in some way the deviation of the excitonic state from the hydrogenic 1s state for which hole distance equals $\langle z_e \rangle$.

The force on the exciton in our model is given by the Hellmann-Feynman theorem[30,7]:

$$F=-\frac{\partial E_{\text{gr}}}{\partial a}=-\left\langle \psi \left| \frac{\partial V}{\partial a} \right| \psi \right\rangle$$

$$=\int_{z>0} dx\, dy\, dz \frac{(z-a)\,|\psi(x,y,z)|^2}{[x^2+y^2+(z-a)^2]^{3/2}} , \tag{26}$$

where $z>0$ defines the half-space geometry of the crystal and $(0,0,a)$ is the position of the hole in Cartesian coordinates. In Eq. (26), E_{gr} and ψ are, respectively, the ground-state energy and wave function. The relationship of Eq. (26) provides an analytical result when the hole is exactly on the wall. In this case, the ground-state wave function is given by

$$\psi(x,y,z)=\frac{1}{(16\pi a_0^5)^{1/2}} e^{-r/2a_0} z , \tag{27}$$

where a_0 is the effective Bohr radius. This is simply the hydrogenic $2p_z$ wave function as discussed before, except that now the normalization is different. Inserting Eq. (27) into Eq. (26) one gets

$$-\left.\frac{\partial E_{\text{gr}}}{\partial a}\right|_{a=0}=\int_{z>0} dx\, dy\, dz \frac{z}{r^3}\,|\psi(x,y,z)|^2$$

$$=\tfrac{1}{8}\mathscr{R}^{\text{eff}}/a_0 , \tag{28}$$

where $\mathscr{R}^{\text{eff}}$ is the effective Rydberg and a_0 is, again, the effective Bohr radius.

This analytical result agrees with the results of Fig. 5 where we have calculated the force by simply taking the derivative of the ground-state energy with respect to the wall distance. As might be expected, the force is maximum when the hole is at a distance of about $1a_0$ from the wall. The energies and the corresponding separation constants of the ground state are given in Table I. The corresponding wave functions may be obtained from Eqs. (8), (15), (16), and (21).

IV. EXCITED STATES

We have already shown in Fig. 2 the energies of the first two excited states as a function of the wall distance. When the hole is located right on the wall the first excited state is triply degenerate and consists of the $3p_z$-, $3d_{xz}$-, and $3d_{yz}$-type hydrogenic states with the energy $E=-\frac{1}{9}\mathscr{R}^{\text{eff}}$ as discussed by Levine.[8] Here, the $3p_x$-, $3p_y$-, and $3d_{xy}$-type states are not allowed as these wave functions do not vanish on the wall. With the hole away from the wall the triply degenerate state splits into a singly degenerate state and a doubly degenerate state, as shown in Fig. 2, with the former having the lower energy. In the limit that the wall is at infinity the singly degenerate $3p_z$-type state slowly changes into a $2s+2p_z$-type state and the $3d_{xz}$- ($3d_{yz}$-) type state changes into a $2p_x$- ($2p_y$-) type state.

In Fig. 6 we show the electronic wave-function contours of the first excited state in the $\phi=0$ plane for four wall distances. In this case, the wave function smoothly changes from the hydrogenic $3p_z$ state with $E=-\frac{1}{9}\mathscr{R}^{\text{eff}}$ to a hydrogenic $2s+2p_z$ state with $E=-\frac{1}{4}\mathscr{R}^{\text{eff}}$ as the hole initially located on the wall is moved away to a large distance. Similar electronic wave-function contours are shown for the doubly degenerate $m=1$ state in Fig. 7. In this case the $3d_{xz}$-type state changes into a $2p_x$-type hydrogenic state when the wall is moved to infinity.

V. COMPARISON WITH PREVIOUS CALCULATIONS

In Fig. 8 we have compared the exact results with the results of Harper and Hilder[4,7] and of Gallardo and Mattis[7] obtained by a Green's-theorem method. Harper and Hilder's method clearly fails when the exciton is near the wall; in fact it yields the isotropic result in the limiting case where the hole is located right on the wall. Gallardo and Mattis[7] have modified this method. They get the exact result when the hole is right on the surface; however, at a small distance away from the wall ($a \lesssim \frac{1}{2}a_0$), the

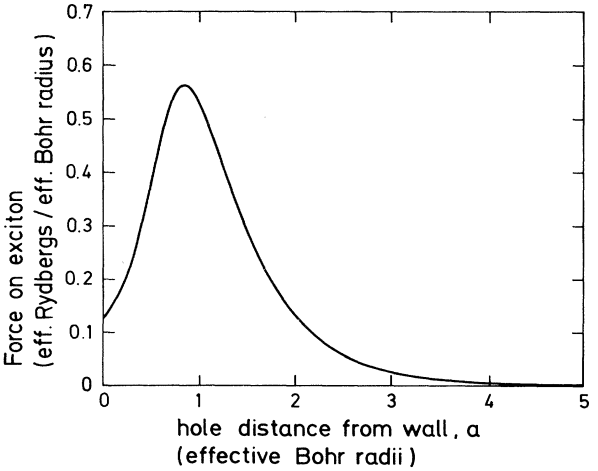

FIG. 5. Force on the exciton, identically equal to $-\partial E_{\text{gr}}/\partial a$, as a function of distance of the hole from the wall. Force is such that it tends to move the exciton away from the wall and into the bulk.

TABLE I. Ground state of the exciton near a rigid wall.

Wall distance a	Binding energy $\|E\|$	Separation constant[a] A'	$d\|E\|/da$
0.00	0.250 000	2.000 000	0.125 00
0.10	0.263 649	1.850 902	0.149 38
0.20	0.280 217	1.703 852	0.183 99
0.30	0.300 917	1.559 351	0.232 66
0.40	0.327 310	1.418 182	0.297 98
0.50	0.360 994	1.281 519	0.377 36
0.60	0.402 865	1.150 940	0.458 95
0.70	0.452 232	1.028 183	0.524 12
0.80	0.506 633	0.914 704	0.558 07
0.90	0.562 698	0.811 314	0.557 94
1.00	0.617 319	0.718 127	0.530 83
1.10	0.668 313	0.634 739	0.487 13
1.20	0.714 496	0.560 454	0.435 87
1.30	0.755 447	0.494 457	0.383 31
1.40	0.791 240	0.435 915	0.333 14
1.50	0.822 218	0.384 036	0.287 22
1.60	0.848 851	0.338 090	0.246 30
1.70	0.871 646	0.297 419	0.210 43
1.80	0.891 096	0.261 433	0.179 34
1.90	0.907 658	0.229 607	0.152 58
2.00	0.921 741	0.201 474	0.129 67
2.50	0.965 983	0.103 256	0.057 00
3.00	0.985 358	0.051 489	0.024 85
3.50	0.993 771	0.024 956	0.010 73
4.00	0.997 384	0.011 769	0.004 57
4.50	0.998 915	0.005 410	0.001 92
5.00	0.999 555	0.002 426	0.000 80
∞	1	0	0

[a] $A' = A + |E|a^2$.

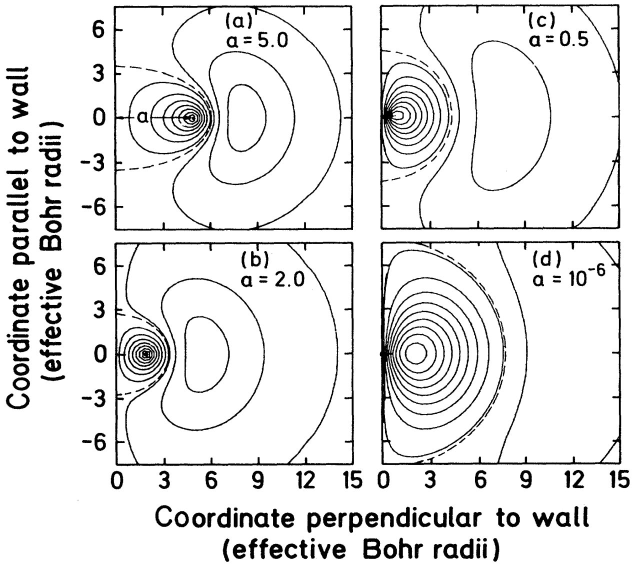

FIG. 6. Electronic wave-function contours of the first excited state for various distances a of the hole from the wall: (a) $a = 5$, (b) $a = 2$, (c) $a = 0.5$, and (d) $a = 10^{-6}$. Distances are in units of a_0. Wave functions vanish on the dashed lines and, of course, also on the wall.

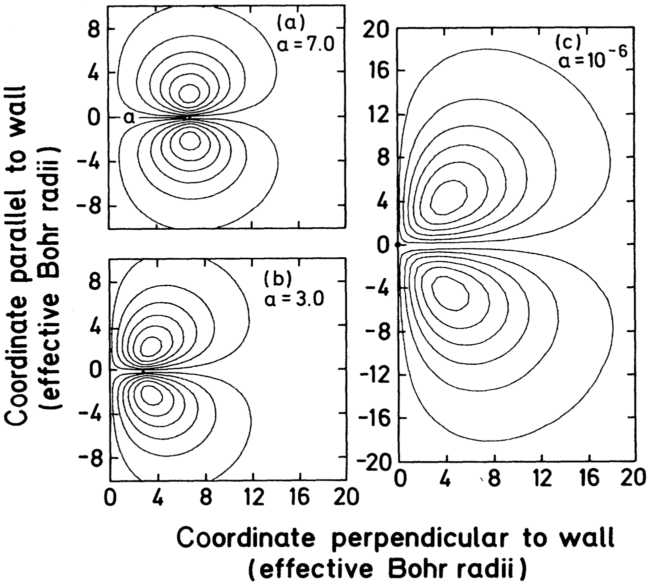

FIG. 7. Electronic wave-function contours of the second excited state for various distances a of the hole from the wall: (a) $a = 7$, (b) $a = 3$, and (c) $a = 10^{-6}$. Distances are in units of a_0. The second excited state is doubly degenerate as has been discussed in the text. In this figure only one of them has been shown.

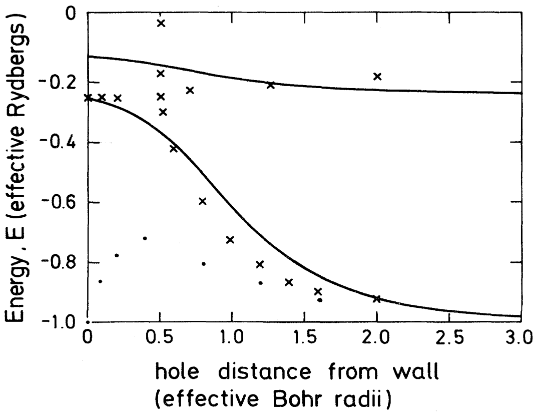

FIG. 8. Comparison of the exact energies with approximate solutions of Harper and Hilder (dots) and of Gallardo and Mattis (crosses).

method is insensitive to the position of the wall. When the hole is more than $\frac{1}{2}a_0$ away from the wall, their method yields a ground-state energy only in qualitative agreement with the exact solution.

VI. CONCLUSION

In conclusion, the exact eigenstates of an exciton near the surface of a semiconductor in the effective-mass approximation and also in the approximation where the hole motion is neglected have been obtained. The ground-state wave function has been studied in some detail, and the way it changes between the two limits—when the hole is deep inside the semiconductor and when it it right on the surface—has been seen. The exact solutions have been compared with some approximate solutions in the literature. It is hoped that this study is helpful in the understanding of the behavior of more realistic excitons, i.e., excitons with a finite hole mass.

Note added in proof. The author has recently received a copy of Z. Liu and D. L. Lin, Phys. Rev. B (in press), which treats the hydrogen atom in semi-infinite space, essentially the problem treated here, by a modified Green's-theorem method. A comparison with the exact results presented here shows that Liu and Lin obtain reasonably accurate energy eigenvalues when the exciton is close ($\lesssim \frac{1}{2}a_0$) to the surface.

ACKNOWLEDGMENTS

The author would like to thank Dr. M. Altarelli, Dr. P. J. Kelly, Dr. M. Springborg, and above all Professor O. K. Andersen for stimulating discussions.

APPENDIX

We present Tables II and III.

TABLE II. First excited state $m=0$.

Wall distance a	Binding energy $\|E\|$	Separation constant[a] A'	$d\|E\|/da$
0.00	0.111 111	2.000 000	0.037 04
0.10	0.115 101	1.850 311	0.043 10
0.20	0.119 805	1.701 312	0.051 40
0.30	0.125 468	1.553 133	0.062 30
0.40	0.132 335	1.405 966	0.075 24
0.50	0.140 509	1.260 060	0.087 91
0.60	0.149 779	1.115 689	0.096 49
0.70	0.159 571	0.973 070	0.098 13
0.80	0.169 184	0.832 301	0.093 23
0.90	0.178 088	0.693 370	0.084 47
1.00	0.186 039	0.556 212	0.074 52
1.10	0.193 008	0.420 752	0.065 00
1.20	0.199 076	0.286 921	0.056 55
1.30	0.204 359	0.154 658	0.049 31
1.40	0.208 974	0.023 911	0.043 17
1.50	0.213 024	−0.105 370	0.037 98
1.60	0.216 596	−0.233 233	0.033 57
1.70	0.219 760	−0.359 723	0.029 81
1.80	0.222 576	−0.484 886	0.026 58
1.90	0.225 092	−0.608 769	0.023 79
2.00	0.227 347	−0.731 415	0.021 36
2.50	0.235 700	−1.327 685	0.012 90
3.00	0.240 841	−1.899 643	0.008 08
3.50	0.244 093	−2.452 256	0.005 16
4.00	0.246 179	−2.989 818	0.003 33
4.50	0.247 528	−3.515 912	0.002 15
5.00	0.248 402	−4.033 440	0.001 40
∞	0.250 000		0.000 00

[a] $A'=A+|E|a^2$.

TABLE III. Second excited state $m=1$.

Wall distance a	Binding energy $\lvert E \rvert$	Separation constant[a] A'	$d\lvert E \rvert/da$
0.00	0.111 111	6.000 000	0.018 52
0.10	0.113 005	5.875 538	0.019 37
0.20	0.114 987	5.752 193	0.020 28
0.30	0.117 063	5.630 027	0.021 25
0.40	0.119 240	5.509 110	0.022 29
0.50	0.121 523	5.389 518	0.023 40
0.60	0.123 921	5.271 335	0.024 56
0.70	0.126 437	5.154 653	0.025 78
0.80	0.129 078	5.039 571	0.027 04
0.90	0.131 845	4.926 197	0.028 32
1.00	0.134 743	4.814 645	0.029 62
1.10	0.137 768	4.705 036	0.030 89
1.20	0.140 919	4.597 495	0.032 12
1.30	0.144 190	4.492 149	0.033 27
1.40	0.147 570	4.389 124	0.034 31
1.50	0.151 047	4.288 541	0.035 21
1.60	0.154 606	4.190 516	0.035 94
1.70	0.158 229	4.095 152	0.036 49
1.80	0.161 897	4.002 539	0.036 83
1.90	0.165 589	3.912 750	0.036 97
2.00	0.169 284	3.825 843	0.036 90
2.50	0.187 137	3.435 288	0.033 85
3.00	0.202 692	3.115 895	0.028 14
3.50	0.215 210	2.859 994	0.021 99
4.00	0.224 807	2.657 637	0.016 57
4.50	0.231 955	2.499 132	0.012 21
5.00	0.237 183	2.375 981	0.008 86
∞	0.250 000		0.000 00

[a] $A' = A + \lvert E \rvert a^2$.

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