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Hydrogenic atom in semi-infinite space

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A variational method is developed to determine the recycling function in a Green's-theorem calculation of the energy levels of a hydrogenic atom in semi-infinite space. It is shown that, with suitable choice of the trial wave function, the problem is reduced to an equivalent one-dimensional eigenvalue problem with eigenvalue ΔE, the energy shift of the bulk levels. The method can be applied to any state, and the three lowest energy levels obtained this way are compared with available existing results. The change of eigenstates as the atom approaches the surface is also discussed.

I. INTRODUCTION

The problem of a hydrogenic atom near a rigid wall is of great interest in surface physics because it recapitulates almost all the properties of the Wannier exciton as well as the shallow states of impurity atoms near the surface. The problem becomes quickly very complicated and requires rather sophisticated theoretical treatment if one intends to include the microscopic structure of the surface. Fortunately, these microscopic complications have little effect in most cases when surface states are ignored. As a particular example, D'Andrea and Del Sole[1] obtained excellent agreement with experiments in their calculation of the normal-incidence reflectivity by treating the exciton simply as a hydrogen atom including the center-of-mass motion.

For the atom located precisely on the surface of a semi-infinite medium, the problem was solved exactly by Levine.[2] Because of the presence of rigid surface, the boundary condition of the problem allows only $n(n-1)/2$ states with $l+m$ odd for each principal quantum number n instead of n^2 states when the atom is in the bulk. He also found many other interesting conclusions which are not directly related to the present work.

When the atom is situated inside the medium but not too far from the surface, it is no longer possible to solve analytically the Schrödinger equation with the proper boundary condition. Harper and Hilder[3] made use of the Green's theorem to recycle the eigenfunction ϕ_{nlm} of the hydrogen atom in the bulk. The shift of energy levels due to the surface calculated this way, however, were satisfactory only when the atom was not close to the surface. In fact, when the atom approaches the surface, the energy levels turn out to be equal to their isotropic values in violation of the boundary condition.

The situation was significantly improved by Gallardo and Mattis[4] who introduced the recycling function $\chi(z)$ such that the true wave function with surface is given by $\psi_{nlm}=\chi\phi_{nlm}$ where ϕ_{nlm} is the hydrogen wave function in the bulk. By choosing suitable forms of χ, they were able to reproduce the correct energy levels at the surface as obtained by Levine. The most obvious defect is probably that the energies are not smooth functions of the distance of the atom from the surface. As a matter of fact, each energy curve is a result of two intersecting curves. For instance, the ground-state energy consists of E_{210} for small distances and E_{100} for large distances. When these two curves intersect, they discard the unwanted parts on the ground of noncrossing energy levels resulting in a kink in the ground-state energy curve at the intersection. Similar situations exist in other energy levels. Futhermore, the energy curves possess positive slope in the neighborhood of the surface. This, as has been noted by the authors themselves, violates the Hellmann-Feynman theorem[5] which requires a negative slope reflecting the repulsive nature of the surface.

Since the method does not involve any adjustable parameter, the result depends solely on the choice of the recycling function χ. Therefore, we reformulate the problem in a way that the energy shift is a functional of the recycling function χ which contains a single parameter. We first minimize the functional to determine the form of the function χ. This variational procedure leads to a one-dimensional eigenvalue problem with the energy shift as the eigenvalue. The equivalent one-dimensional potential energy in this equation has no singularity throughout the half-space and hence the equation can be solved numerically for minimum energy shift by adjusting the parameter. Thus we have obtained the energy levels that are free of all the deficiencies mentioned above at the expense of introducing one adjustable parameter.

In Sec. II we formulate the problem and show how it is reduced to an equivalent one-dimensional equation. Section III is devoted to the calculation of ground-state energy and the excited states are treated in Sec. IV. In Sec. V we give a brief discussion of our results and some related questions that are of more general nature.

II. FORMULATION OF THE PROBLEM

For an atom whose center of mass is located at $(0,0,z_0)$ in the semi-infinite space, the Schrödinger equation can be written as

$$(-\nabla^2+V)\Psi(x,y,x)=E\Psi(x,y,z)\ , \qquad (1)$$

with the boundary condition

$$\Psi(x,y,0)=0 \ , \tag{2}$$

where we have chosen the z axis to be perpendicular to the surface. While the validity of the boundary condition (2) is still an open question as has been discussed in great detail by D'Andrea and Del Sole, we nevertheless still assume it here as they did to avoid the excessive complications due to the microscopic structure of the surface. This boundary condition has been shown to be correct in the absence of surface states when a large surface barrier prevents electron and hole escape from the surface.[6,7] It has also been derived[8] from the image-potential infinite barrier that electrons and holes experience approaching the surface.

In Eq. (1) we have used the atomic units, i.e., the first Bohr radius $a_0=\epsilon\hbar^2/\mu e^2$ for length and the Rydberg $R_\infty=\mu e^4/2\epsilon^2\hbar^2$ for energy. Accordingly, the potential-energy operator is given by

$$V=\begin{cases}-2[x^2+y^2+(z-z_0)^2]^{-1/2}, & z>0\\ \infty, \ z\le 0 \ . \end{cases} \tag{3}$$

The image potential caused by the surface has been ignored because its inclusion in addition to (2) has been shown to yield negligible effect.[9] The corresponding Schrödinger equation for an atom in full space is

$$\left[-\nabla^2-\frac{2}{r}\right]\phi(\vec{r})=E'\phi(\vec{r}) \ , \tag{4}$$

with the usual boundary condition that $\phi(\vec{r})=0$ as $r\rightarrow\infty$.

To find the energy shift due to the rigid wall, we write, as in Gallardo and Mattis,[4]

$$\Psi(x,y,z)=\chi(x,y,z)\phi(\vec{r}) \ , \tag{5}$$

and require the boundary condition

$$\chi(x,y,0)=0 \ . \tag{6}$$

Although the rigid wall destroys the spherical symmetry of the problem, it preserves the symmetry under rotation about the z axis. This means that the orbital angular momentum l is no longer a good quantum number while m still is. Hence the recycling function χ introduced in (6) does not change the eigenfunction $e^{im\phi}$ and is therefore a real function.

Substituting (5) in (1), we obtain

$$-2\phi^*\vec{\nabla}\phi\cdot\vec{\nabla}\chi-|\phi|^2\nabla^2\chi=\Delta E\,|\phi|^2\chi \ , \tag{7}$$

where $\Delta E=E-E'$ is the correction to energy level caused by the rigid surface at $z=0$. Taking the complex conjugate of (7) and adding them up, we find

$$\vec{\nabla}\cdot(|\phi|^2\vec{\nabla}\chi)=-\Delta E\,|\phi|^2\chi \ . \tag{8}$$

Integrating (8) over space with the boundary condition (6) and applying Green's theorem, we have

$$\Delta E=-\frac{\int\phi^*\vec{\nabla}\Psi\cdot d\vec{S}}{\int\phi^*\Psi\,d^3r} \ . \tag{9}$$

This is the formula used by Harper and Hilder and by Gallardo and Mattis to calculate ΔE by choosing simple forms of the recycling function χ. Instead of (9), we multiply (8) by χ and integrate over the half-space to obtain

$$\Delta E[\chi(\vec{r})]=\frac{\int d^3r\,|\phi|^2(\vec{\nabla}\chi)^2}{\int d^3r\,|\phi|^2\chi^2} \ , \tag{10}$$

where we have made use of the boundary condition (6) to drop out the integrated term on the left-hand side. It is not difficult to show that (8) is the Euler equation of (10) if we regard ΔE as a functional of the function χ. Hence we can apply the variational method to calculate the energy change by minimizing the functional ΔE in Eq. (10). We choose the trial function

$$\chi=e^{\lambda r}Q(z) \ , \tag{11}$$

where $\lambda=\lambda(z_0)$ is a parameter to be determined by the minimum value of ΔE and

$$r=[x^2+y^2+(z-z_0)^2]^{1/2} \ .$$

Substituting (11) into (10) we obtain, after a simple calculation,

$$\Delta E=\frac{\int_0^\infty dz\left\{f_1(z)\left[\lambda^2Q^2+\left[\frac{dQ}{dz}\right]^2\right]+2\lambda(z-z_0)f_2(z)Q\frac{dQ}{dz}\right\}}{\int_0^\infty dz\,f_1(z)Q} \ , \tag{12}$$

where we have defined

$$f_1(z)=\int|\phi|^2e^{2\lambda r}dx\,dy \ , \tag{13a}$$

$$f_2(z)=\int|\phi|^2\frac{e^{2\lambda r}}{r}dx\,dy \ . \tag{13b}$$

We are now ready to apply the variational principle to the functional ΔE due to changes in the function $Q(z)$, noting that $\Delta Q=0$ at both ends. The standard procedure leads to the Euler equation,

$$-\frac{d}{dz}\left[f_1\frac{dQ}{dz}\right]-\lambda\left[f_2+(z-z_0)\frac{df_2}{dz}\right]Q+\lambda^2f_1Q=\Delta E\,f_1Q \ . \tag{14}$$

If we now introduce another function $W(z)$ defined by

$$Q(z)=f_1^{-1/2}W(z) \ , \tag{15}$$

we can rewrite (14) in the form of a one-dimensional Schrödinger equation,

$$\left[-\frac{d^2}{dz^2}+U\right]W=\Delta E\,W \ . \tag{16a}$$

In order that the solution reproduces the exact form of Ψ in the limiting cases $z_0=0$ and $z_0\rightarrow\infty$, we impose the boundary conditions

$$W(0)=W(\infty)=0 \ . \tag{16b}$$

In (16a), the equivalent potential energy U is given by

$$U=\frac{1}{2}\frac{f_1''}{f_1}-\frac{1}{4}\left[\frac{f_1'}{f_1}\right]^2 -\lambda\left[\frac{f_2}{f_1}+(z-z_0)\frac{f_2'}{f_1}\right]+\lambda^2\,, \tag{17}$$

where the prime means derivative of the function with respect to z. The normalization of the wave function W is, from (5), (11), and (15), given by

$$\begin{aligned}\int |\Psi|^2 d^3r &= \int_0^\infty dz\, Q^2 \int dx\, dy\, e^{2\lambda r}|\phi|^2 \\ &= \int_0^\infty dz\, Q^2 f_1 \\ &= \int_0^\infty W^2 dz = 1\,. \end{aligned} \tag{18}$$

III. GROUND STATE

For the ground state, we require that the wave function

$\Psi \to \phi_{210}$ as $z_0=0$

$\Psi \to \phi_{100}$ as $z_0 \to \infty$.

Thus the parameter $\lambda(z_0)$ in Eq. (11) starts from the value $\frac{1}{2}$ at $z_0=0$ and changes to zero as $z_0 \to \infty$. The function Q, on the other hand, must approach to z at $z_0=0$ and $Q \to 1$ as $z_0 \to \infty$. Using the hydrogen ground-state wave function ϕ_{100} in (13) we find

$$f_1 = Ae^{-2(1-\lambda)z_1}\left[z_1+\frac{1}{2(1-\lambda)}\right], \tag{19a}$$

$$f_2 = Ae^{-2(1-\lambda)z_1} \tag{19b}$$

where $z_1 \equiv |z-z_0|$ and A is just a constant. With f_1 and f_2 given by (19) we find from (17) the equivalent potential energy

$$U = 1-\frac{1+\lambda}{z_1+1/2(1-\lambda)} -\frac{1}{4[z_1+1/2(1-\lambda)]^2}\,. \tag{20}$$

In Fig. 1, we plot U as a function of z_1 for the two limiting cases. It is found that in general the potential U has a minimum at the origin for any finite z_0. The minimum value changes smoothly from -2 to -0.75 when the atom moves in from infinite to the surface. As $z_1 \to \infty$, $U \to 1$ for all λ. It is a smooth continuous function with a discontinuity in its derivative at the origin. When λ increases from zero, the potential well depth decreases and at the same time its width increases. Consequently, the atom provides less binding and the wave function spreads wider, reflecting the repulsive effect of the wall as the atom approaches it.

It is a simple matter to verify that when $z_0=0$, Eqs. (16) has exact normalized eigenfunction,

$$W=\frac{1}{2\sqrt{2}}z(z+1)^{1/2}e^{-z/2}\,, \tag{21}$$

with eigenvalue $\Delta E=\frac{3}{4}$. This implies that the ground-state energy of the atom located at the surface is $-\frac{1}{4}$, an exact result. As $z_0 \to \infty$. Equations (16) also yield the exact solution

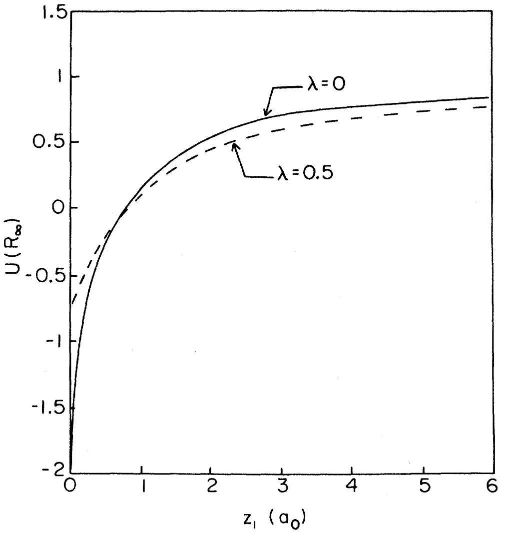

FIG. 1. Two limiting cases of the one-dimensional equivalent potential for the ground state.

$$W=(z_1+\tfrac{1}{2})^{1/2}e^{-z_1}\,, \tag{22}$$

with eigenvalue $\Delta E=0$.

For an arbitrary finite z_0, however, the equation has to be integrated numerically. We look for solutions to Eqs. (16) with the equivalent potential energy given by (20). The calculation involves the following steps. We first adjust ΔE for a given λ to find $W(z)$ which satisfies the boundary conditions (16b) in a manner similar to that described in Kramers.[10] Then we repeat the procedure by changing the value of λ in the range $0<\lambda<\frac{1}{2}$ to obtain ΔE as a function of λ. The eigenvalue and corresponding eigenfunction are determined by the minimum of the

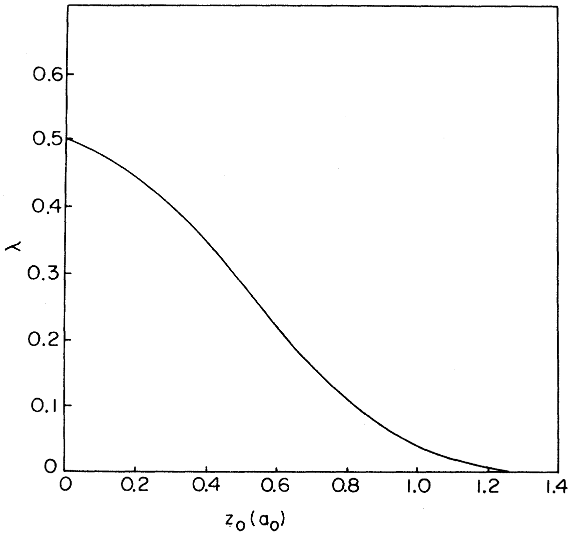

FIG. 2. Variation of the parameter for the ground state as a function of the distance z_0.

function $\Delta E(\lambda)$. The parameter λ for ground state determined by the minimum value of ΔE for different z_0 is plotted in Fig. 2 as a function of z_0 and the ground-state energy calculated this way is shown in Fig. 3 along with other existing results for comparison. It is observed that the energy increases smoothly all the way as z_0 decreases and approaches the surface with a negative slope as required by the Hellmann-Feynman theorem.

IV. EXCITED STATES

From the above calculation of the ground state, we observe that the success of our method depends upon the fact that the recycling function can be put in the form of (11). This form of χ then leads naturally to the explicit form of the equivalent potential U in (16) as well as the exact solution for the limiting cases $z_0=0$ and $z_0 \rightarrow \infty$. It turns out that this is often not as simple in the case of excited states. For a given principal quantum number n, only $n(n-1)/2$ states with $l+m$ odd survive as the atom approaches the surface, all other levels are presumably squeezed into the continuum.[4] Our method described above can be applied directly to Levine levels of largest allowed $|m|$, namely, $m=n-2$. For a Levine level specified by $(n, l=n-1, |m|<n-2)$, we have to construct a more complicated trial wave function.

Consider, for example, the first excited state ϕ_{310}. One may try

$$\Psi=\chi\phi=e^{\lambda r}Q(z)(\beta+r)e^{-r/2} \tag{23}$$

by introducing another parameter β which assumes the value 2 for large z_0 and increases to 6 at $z_0=0$. Unfortunately, $\phi=(\beta+r)e^{-r/2}$ is not an eigenstate of the hydrogen atom in the bulk and one cannot apply the Green's theorem method to calculate ΔE. To resolve this difficulty, we propose

$$\Psi_{nlm}=\chi\Phi \tag{24}$$

with

$$\Phi=\phi_{n-1,l-1,m}+\sum_{\nu}\xi_\nu(z,r,\lambda)\phi_\nu(\vec{r}) , \tag{25}$$

where $\xi_\nu(r,z_1,\lambda)$ are required to vanish as $\lambda \rightarrow 0$ or $z_0 \rightarrow \infty$ on one hand and to recover the Levine state as $z_0=0$ on the other. The subscript ν stands for the set of quantum numbers needed to specify the hydrogen wave function and the summation may run over all the sublevels of the same m within the $(n-1)$th shell including $\phi_{n-1,l-1,m}$. Just which states are involved in the sum will depend on the Levine level in question. The main point is that the function Ψ_{nlm} reproduces an exact solution on the surface and in the bulk, and at the same time the parameter β in ϕ can be expressed in terms of λ by means of the expression (25). It may be pointed out in passing that although levels of opposite m are still degenerate for all z_0 as can be seen from time reversal invariance, they do not mix because of the symmetry mentioned earlier.

In the following we shall outline how the Green's theorem method must be modified to accomodate the extra terms in (25). Equations (1)–(4) remain unchanged. The ϕ's appearing in (25), being wave functions for the sublevels within the same shell, all satisfy (4) with the same energy E'. Hence the substitution of (24) in (1) leads to, after a little algebra,

$$-2\Phi^*\vec{\nabla}\Phi\cdot\vec{\nabla}\chi-|\Phi|^2\nabla^2\chi-\chi\Omega\Phi^*=\Delta E\,|\Phi|^2\chi , \tag{26}$$

where

$$\Omega=\sum_{\nu}(\phi_\nu\nabla^2\xi_\nu+2\vec{\nabla}\xi_\nu\cdot\vec{\nabla}\phi_\nu)$$
$$=\sum_{\nu}\left[\nabla^2(\xi_\nu\phi_\nu)+\left[E'+\frac{2}{r}\right]\xi_\nu\phi_\nu\right] . \tag{27}$$

Taking the complex conjugate of (26) and adding to it, one obtains

$$\vec{\nabla}\cdot(|\Phi|^2\vec{\nabla}\chi)+\chi\,\mathrm{Re}(\Phi\Omega^*)=-\Delta E\,\chi\,|\Phi|^2 , \tag{28}$$

where Re means the real part of a complex function. Multiplying (28) by χ and integrating over the half-space, one finds

$$\Delta E=\frac{\int[\,|\Phi|^2(\vec{\nabla}\chi)^2-\chi^2\mathrm{Re}(\Phi\Omega^*)]d^3r}{\int|\Phi|^2\chi^2d^3r} , \tag{29}$$

where use has been made of Green's theorem as well as the boundary condition (6). Again one can show without difficulty that (28) is the Euler equation of the functional (29).

Using the definition (11), one then applies the variational principle to the functional ΔE by varying the funtion Q with $\Delta Q=0$ at both ends. This yields

$$-\frac{d}{dz}\left[f_1\frac{dQ}{dz}\right]+\left[\lambda^2 f_1-\lambda\left[f_2+(z-z_0)\frac{df_2}{dz}\right]-f_3\right]Q=\Delta E\,f_1Q , \tag{30}$$

where f_1 and f_2 are given by (13) with ϕ replaced by Φ and f_3 is defined by

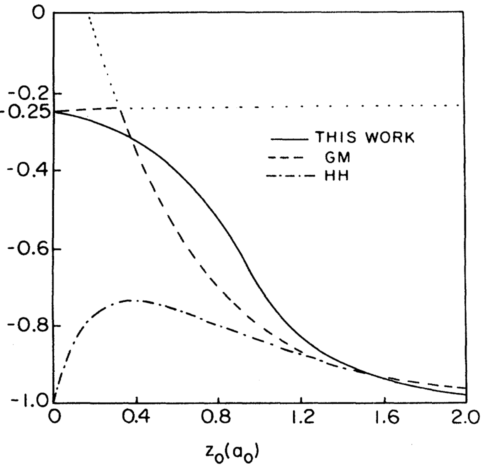

FIG. 3. Comparison of the ground-state energy calculated in this work with those obtained by Gallardo and Mattis (GM) and by Harper and Hilder (HH). The dotted line indicates that part discarded in GM.

$$f_3=\int e^{2\lambda r}\mathrm{Re}(\Phi\Omega^*)dx\,dy\ . \tag{31}$$

The equivalent one-dimensional equation (16) follows directly if one uses (15) with the equivalent potential energy operator given by

$$U=\frac{1}{2}\frac{f_1''}{f_1}-\frac{1}{4}\left[\frac{f_1'}{f_1}\right]^2-\lambda\left[\frac{f_2}{f_1}+(z-z_0)\frac{f_2'}{f_1}\right]-\frac{f_3}{f_1}+\lambda^2\ . \tag{32}$$

Thus we choose, for the first excited state,

$$\Phi=\phi_{200}+\xi_{210}\phi_{210}=[2-(1-7\lambda+18\lambda^2)r]e^{-r/2}\ , \tag{33}$$

where

$$\xi_{210}=\lambda(7-18\lambda)r/(z-z_0)\ . \tag{34}$$

With the definition (11), our trial function is then

$$\Psi=e^{\lambda r}Q(z)\Phi\ . \tag{35}$$

It can readily be verified that Ψ reduces to the exact wave function at the surface and in the bulk if the parameter λ varies from $\frac{1}{6}$ at $z_0=0$ and decreases to zero as $z_0\to\infty$, while the function $Q(z)$ behaves like z at the surface and approaches a constant as $z_0\to\infty$. The equivalent potential energy can be calculated from (32) by evaluating the f's with the function Φ given by (33). The calculation is tedious but straightforward and the result is

$$U=-\frac{1}{4}\left[\frac{F'}{F}\right]^2-\frac{K}{F}+\frac{1}{4}\ , \tag{36}$$

where F' is the first derivative with respect to z_1 and

$$F=z_1^3-\frac{1+13\lambda-54\lambda^2}{(1-2\lambda)(1-7\lambda+18\lambda^2)}z_1^2+\frac{2(1-14\lambda+135\lambda^2-612\lambda^3+972\lambda^4)}{(1-2\lambda)^2(1-7\lambda+18\lambda^2)^2}z_1+\frac{2(1-14\lambda+135\lambda^2-612\lambda^3+972\lambda^4)}{(1-2\lambda)^3(1-7\lambda+18\lambda^2)^2}\ , \tag{37}$$

$$K=(\tfrac{3}{2}+\lambda)z_1^2-\frac{2(2+\lambda-8\lambda^2-36\lambda^3)}{(1-2\lambda)(1-7\lambda+18\lambda^2)}z_1+\frac{2(1+6\lambda)(1-3\lambda+\lambda^2-36\lambda^3+108\lambda^4)}{(1-2\lambda)^2(1-7\lambda+18\lambda^2)^2}\ . \tag{38}$$

Substituting (36) in (16) and remembering (15), we have the equivalent one-dimensional equation which can then be solved numerically for ΔE.

The next state that survives at the surfaces is ϕ_{321}. The trail wave function is

$$\Psi=\chi\phi_{211}=e^{\lambda r}Q(z)\phi_{211}\ , \tag{39}$$

which recovers the exact solution at $z_0=0$ if $\lambda=\frac{1}{6}$ and $Q=z$. Thus λ increases from zero to $\frac{1}{6}$ as the atom approaches the surface from infinity. The equivalent one-dimensional potential energy is again of the form of (36) with

$$F=z_1^2+\frac{3z_1}{1-2\lambda}+\frac{3}{(1-2\lambda)^2} \tag{40}$$

and

$$K=(1+2\lambda)z_1+\frac{1+6\lambda}{2(1-2\lambda)}\ . \tag{41}$$

The procedure of numerical calculation of the energy shift ΔE is the same as in the case of the ground state. We plot the first two excited-state energies vs z_0 in Fig. 4 and the variation of the parameter λ as a function of z_0 is plotted in Fig. 5 for these two states. It should be noted that states with m and $-m$ are still degenerate in the presence of the surface. Hence a single curve corresponds to $m=\pm 1$ in these figures.

Energy levels of any arbitrary excited states can be calculated by this method in a straightforward way. The algebra may become more involved as one goes to higher levels but remains elementary. In fact, the one-dimensional equivalent potential-energy operator corresponding to any Levine state with principal quantum number n is given by

$$U_n=\frac{1}{(n-1)^2}-\frac{K}{F}-\frac{1}{4}\left[\frac{F'}{F}\right]^2\ , \tag{42}$$

where F and K are determined by the wave function Φ through the f's as we have illustrated in the above two cases. The equivalent potentials U_4 for levels in the next shell have been worked out but numerical calculation has not been performed because of the lack of practical interest.

V. DISCUSSION

We have applied variational principle to determine the recycling function in the Green's-theorem method for cal-

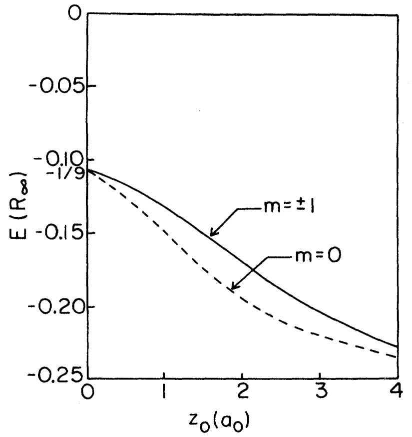

FIG. 4. Energy of the first excited state. Note that the degeneracy is partially lifted by the surface.

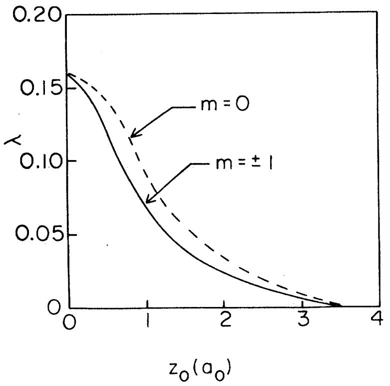

FIG. 5. Parameter λ for the first two excited states.

culating the energy shift of a hydrogenic atom caused by the surface. All energy levels can be calculated as a function of distance of the atom from the surface. They are all continuous smooth curves giving exact energies at both ends. It appears in general that the bulk state $\phi_{n-1,l-1,m}$ changes gradually into the Levine state ϕ_{nlm} as the atom reaches the surface. Physically one might think that the influence of the surface on the wave function would not be so severe in the xy plane as in the z direction that the number of peaks of the probability distribution would not change.

Recently, Lee and Mei[11] developed a perturbation method using pseudopotential technique to calculate the energy shift for z_0 greater than the atomic radius in the state under consideration and found that states in the continuum contribute significantly to the bound state in question as the atom moves toward the surface. However, nothing can be said about the change in wave function as z_0 decreases further.

Since $l+m$ is odd for all Levine states, all the bulk states with $l+m$ odd must disappear near the surface. They are presumably pushed into the continuum as has been pointed out by Gallardo and Mattis[4] who have also given an argument to discuss the level crossing when z_0 is small. To our knowledge, there is no theory up to this time that predicts when and how these states disappear into the continuum. We have, however, tried to trace the state ϕ_{210} numerically from large z_0 toward the surface. As we have discussed previously, for a fixed z_0 the eigenvalue ΔE of Eq. (16) is determined by the value of λ which minimizes ΔE. This can be done until $z_0 \approx 4$. When $z_0 \leq 4$, no extremum ΔE was found for all physically allowed λ. Since the probability $|\phi_{210}|^2$ peaks at around $z_1 = z - z_0 \approx 4$, it is not unreasonable to conclude that the bulk states with $l+m$ odd start to disappear as the atom approaches to a distance z_0 of the order of the atomic radius in that state.

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