Variational solutions of simple quantum systems subject to variable boundary conditions. I. A model for physisorption[a)]

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A variational solution to a model problem of a hydrogen atom near a sharp planar surface of a semi-infinite substrate is studied. Results are presented for the ground and excited eigenstates and dipole moments of the hydrogen atom as a function of distance from the surface for two models: (a) a system in which the half-space occupied by the solid is represented by an infinite potential step; and (b) a system in which the semi-infinite substrate is perfectly imaging subject to a boundary condition that excludes the atomic electron from the substrate. Model (b) is considered as an idealized model for physisorption, where the exclusion of the electron simulates the exchange repulsion originating from the overlap of the atomic and substrate electrons. Results for the physisorption holding potential as a function of distance from the plane are presented and discussed.

Boundary conditions, as utilized in quantum mechanics, are usually dictated by the requirements of *physical admissibility*. For example, when considering bound states the requirement that the normalization integral converge leads to the consideration of only those solutions which are regular at the origin and are zero at infinity. For scattering states a wave function which tends to infinity as r goes to infinity corresponds to a state that has no physical meaning and must be discarded. More generally it is known that a partial differential equation possesses several arbitrary constants and it is the specification of the value of the solution, or its normal derivative, on the boundary that yields the values of these constants.

One of the first uses of a boundary perturbation, that is a change in the boundary conditions, to *model* a physical situation was a calculation of the energy levels of a compressed hydrogen atom.[1,2] In this calculation the effect of very high pressure on atomic hydrogen is taken into account by requiring that the wave function vanish on a sphere at some finite distance from the proton. This type of calculation is, of course, only an approximate one for it only indicates the effect of repulsive forces at very high densities; but of course this is the main attraction of such an approximation in that it replaces the complicated set of interactions with only a change in the boundary conditions, which in this case is exactly solvable.[3]

By changing the new boundary surface from the sphere of the previous example to an infinite plane surface, there results a situation that has been used to model several physical systems. In particular, the requirement of a vanishing wave function on a plane has been used[4] to represent the exchange repulsion of atomic hydrogen physically adsorbed onto a surface.

Perhaps a more realistic use of this boundary condition in the modeling of a physical problem arises in the effective mass theory of shallow donor impurities near the surface of a semiconductor or a semiconductor–oxide interface. Because the binding energy of a shallow donor is of the order of a few meV and the height of the surface barrier is several eV, the surface is essentially an infinite potential barrier and the envelope function of the donor impurity must be required to vanish on the surface. This condition on shallow impurities near semiconductor surfaces was first pointed out by Levine[5(a)] and Gadzuk.[5(b)]

It is the last two examples of modeling a physical problem with the use of boundary conditions that will be addressed in this series. The boundary perturbation in each case involves a change in the shape of the boundary surface while still requiring that homogeneous Dirichlet conditions be satisfied. (Recall that the isolated hydrogen atom wave function is required to be zero on the sphere at infinity.)

When the surface on which the boundary conditions are to be specified is no longer a surface in a coordinate system in which the partial differential equation separates, the problem is nonseparable. This is due to the fact that even though it may be possible to separate the equation, there is no way to satisfy the boundary conditions on a surface which depends upon at least two independent variables. Because of this nonseparability, some type of approximation method must be used.

One of the first approaches to the boundary perturbation problem was made by Brillouin.[6] By considering a displacement operator acting on the boundary he was able to construct a method that is formally similar to the standard perturbation series. However, the expansion parameter in this case is the magnitude by which the boundary surface is displaced and this parameter is assumed to be small. This is clearly not satisfied by the problems we wish to solve. Other methods of treating boundary perturbations have been developed[7,8] but they all have the same restriction. That is, they can only be used when the domain of the PDE is finite and the change in the boundaries is finite. In addition to these methods, a perturbation method using Green's functions has been developed by Feshbach[9] and also discussed by Morse and Feshbach.[10] However, the method is mathematically complicated and for the problem of a change in the boundary shape while requiring homogeneous Dirichlet conditions to hold, the method cannot be used to find corrections to the energy beyond the second order.

These considerations lead to the conviction that the

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variational method will yield the best approximate solutions to this type of boundary perturbation problem.

In this paper a variational solution to the problem of a hydrogen atom in the presence of a planar infinite-potential wall is given. The effect of this boundary perturbation on the spectrum of the hydrogen atom is discussed. At a large distance from the plane, the isolated hydrogen atom levels are regained. When the proton lies on the boundary plane the problem is again exactly solvable[5] and these solutions are recovered by the variational solution. Between these two limits the energy levels vary smoothly and exhibit several interesting level crossings. By using these methods, a model advanced by Bruch and Ruijgrok[4] of the physisorption of atomic hydrogen is revisited and information with regard to excited states of the system is provided.

In a subsequent paper[11] in this series we address the problem of a shallow donor impurity near a semiconductor surface or interface. Modifications in the variational solution due to the effect of an anisotropic effective mass are presented. Energy levels of the ground and excited states of shallow donors near the surfaces of silicon and germanium are calculated. One of the results of this model is that the total interaction energy of a shallow donor with the semiconductor surfaces possesses a minimum and this suggests a possible clustering of these impurities near the surface. Finally, the binding energy of a shallow donor impurity associated with an n-type inversion layer of a metal–oxide-semiconductor field effect transistor is calculated and compared with other recent theoretical treatments and experimental results.

The variational method of solution is described in Sec. I where results for the spectrum of a hydrogen atom near an impenetrable wall are given. The introduction of images in a model of physisorption is described in Sec. II and a detailed discussion of the eigenvalue spectrum and energetics of the system is given.

I. VARIATIONAL SOLUTION—HYDROGEN NEAR AN IMPENETRABLE WALL

The variational method of solution is introduced by considering a hydrogen atom which is at some finite distance, say R, from an infinite plane surface upon which the potential is taken to be infinite. This infinite potential manifests itself by the requirement that ψ, the wave function of the electron, must vanish on the plane and in the half-space not containing the proton. In our treatment of the model, the Born–Oppenheimer approximation shall be used, inasmuch as the proton will be taken as being located at a fixed distance from the plane, so that there is no coupling between the nuclear and electronic motions.

The Hamiltonian of the problem is given by the usual hydrogen atom Hamiltonian

$$H = \frac{-h^2}{2m}\nabla^2 - \frac{e^2}{r}, \tag{1.1}$$

but now the boundary condition is that ψ must be equal to zero on the plane $z = R$ (see Fig. 1). This choice of orientation of the plane and coordinate system, which is centered on the proton, is made to simplify the following calculations.

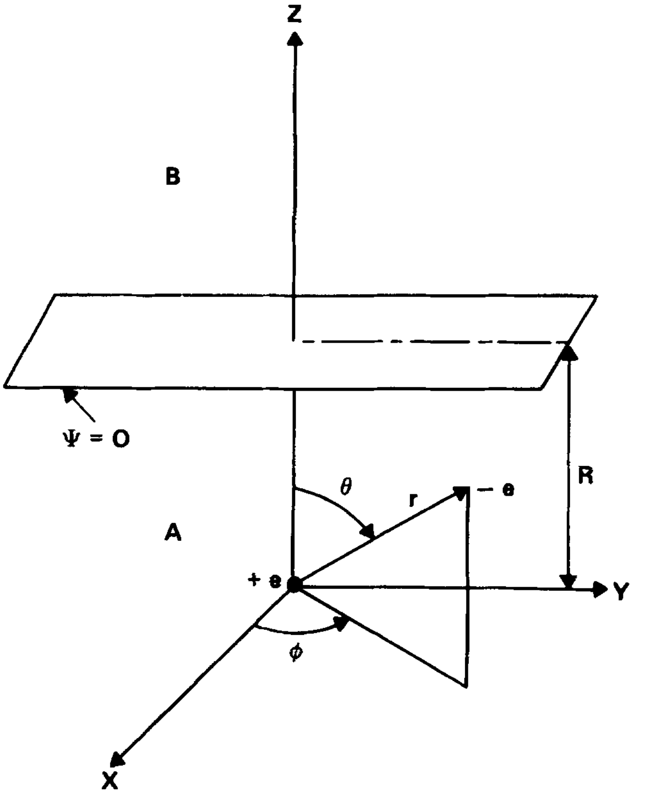

FIG. 1. The coordinate system of Eq. (1.1) centered at the proton and the boundary surface at $z = R = r\cos\theta$.

The variational principle for eigenvalues[12] is

$$\delta[E] = \delta\left[\frac{\int \psi^* H\psi\, dV}{\int \psi^*\psi\, dV}\right] = 0, \tag{1.2}$$

where H is an arbitrary Hermitian operator and this leads to the eigenvalue equation

$$H\psi = E\psi \tag{1.3}$$

only when the function ψ in Eq. (1.2) obeys the same boundary conditions that are to be imposed upon the solutions of Eq. (1.3). In practical applications of the variational method, this means that the trial functions must obey the correct boundary values, independent of the choice of values of whatever variational parameters the trial function may contain. When this condition is satisfied, the trial function is said to be admissible.[13]

This requirement usually poses no problems and its importance is not often emphasized. However, in the present case when the location of the boundary surface is to be varied, and more generally when the boundary surface and conditions will be considered to be input variables, the construction of admissible trial functions can become quite cumbersome. To avoid this complication in the construction of a set of trial functions for the linear variation problem one can form the combination

$$\psi(F) = G(\mathbf{r})\sum_n A_n\phi_n(\mathbf{r}) + F(\mathbf{r}). \tag{1.4}$$

Here the A_n are the linear variation parameters and the set $\phi_n(r)$ is to satisfy the boundary conditions of the unperturbed problem. The n's are taken to stand for all the quantum numbers which characterize the basis set of the system. The function $G(\mathbf{r})$ is such that $G(\mathbf{r}\text{ on }S) = 0$ where S denotes the boundary surface. The function $F(\mathbf{r})$ is to satisfy

$$F(\mathbf{r}\text{ on }S) = X_1(S)$$

for Dirichlet conditions, or

$$\frac{\partial F}{\partial n}(\mathbf{r}\text{ on }S) = X_2(S)$$

for Neumann conditions. In the present instance we are concerned only with homogeneous Dirichlet conditions and therefore need only consider, taking into account the coordinate system of Fig. 1 and the fact that the additional boundary surface is a plane, the combination

$$\Psi(\mathbf{r}) = G(z)\sum_n A_n\phi_n, \tag{1.5}$$

where $G(R) = 0$.

When the boundary surfaces are changed, there arises one more modification of the variational principle of Eq. (1.2). The range of the integrations in Eq. (1.2) is over the domain of the Eq. (1.3) and that domain is defined as the inside of the closed boundary surface on which the boundary conditions are to be satisfied. The fact that the surface is closed follows from the elliptic character of the time-independent Schrödinger equation. This means that the limits of integration in Eq. (1.2) will become dependent upon the position of the boundary surface.

Taking into account all of these considerations and using the trial function of Eq. (1.5) the expectation value for the energy of the system can be written as

$$[E] = \frac{\int_T \left[G(z)\sum_n A_n\phi_n\right]^* H \left[G(z)\sum_n A_n\phi_n\right] dV}{\int_T \left[G(z)\sum_n A_n\phi_n\right]^* \left[G(z)\sum_n A_n\phi_n\right] dV}, \tag{1.6}$$

where the subscript T on the integrals indicates that the integration is over a truncated space and H is given by Eq. (1.1). The basis set used to expand the trial function will not in general be orthogonal, because of the factor $G(z)$ and the integration is over a truncated space, so that the variation of the linear parameters A_n will lead to a generalized matrix eigenvalue problem

$$\mathbf{HA} = E\mathbf{NA}, \tag{1.7}$$

where there now appears the overlap matrix $\mathbf{N}$. More specifically the matrix elements are given by

$$(\mathbf{H})_{n'n} = \int_T [G(z)\phi_{n'}]^* H [G(z)\phi_n] dV \tag{1.8}$$

and

$$(\mathbf{N})_{n'n} = \int_T [G(z)\phi_{n'}]^* [G(z)\phi_n] dV. \tag{1.9}$$

Since both H and N are Hermitian, the usual properties of Hermitian matrices apply; except that the orthonormality of the vectors $\mathbf{A}_n$ is expressed as[14]

$$(\mathbf{A}^\dagger\mathbf{NA})_{nn'} = \delta_{nn'}. \tag{1.10}$$

Before the choice of the set ϕ_n is presented, the specific form of $G(z)$ which is zero on the boundary surface will be given. The most convenient choice is simply to set

$$G(z) = R - z = R - r\cos\theta. \tag{1.11}$$

Then the development of the Laplacian of the Hamiltonian (1.1) is

$$\nabla^2[(R - r\cos\theta)\phi_n] = (R - r\cos\theta)\nabla^2\phi_n - 2\hat{k}\cdot\nabla\phi_n,$$

since, on noting that $\hat{k}$ is the unit vector in the z direction,

$$\nabla(R - r\cos\theta) = -\hat{k}$$

and

$$\nabla^2(R - r\cos\theta) = 0.$$

It is interesting to note that this choice yields an expression that is similar to the variational principle for unrestricted trial functions (i.e., they do not obey the boundary conditions) given by Morse and Feshbach.[10] Both forms involve the derivative of ϕ_n that is normal to the boundry surface; however in the present instance the integration is over the entire volume and not only over the new boundary surface.

The basis set $\phi_n(\mathbf{r})$, which must satisfy only the isolated hydrogen atom boundary conditions, i.e., $\psi \to 0$ as $r \to \infty$, is chosen to be

$$\begin{aligned}\phi_n &\equiv \phi_{nlm}(\mathbf{r},\beta)\\ &= (2\beta)^{3/2}/\sqrt{2n}\,[(N-l-1)!/[(N+l)!]^3]^{1/2}\\ &\quad\times(2\beta r)^l L_{n-l-1}^{2l+1}(2\beta r)e^{-\beta r}Y_l^m(\theta,\phi).\end{aligned} \tag{1.12}$$

In Eq. (1.12) the Y_l^m are the usual spherical harmonics, the L_p^k are the associated Laguerre polynomials and r is taken to be in units of Bohr radius a_0,

$$a_0 = \hbar^2/me^2.$$

This corresponds to a scaling of the Hamiltonian (1.1) to

$$\left(-\nabla^2 - \frac{2}{r}\right)\Psi = E\Psi,$$

where E is given in units of Rydbergs $(e^2/2a_0)$.

The difference between the set of functions given by Eq. (1.12) and the isolated hydrogen atom eigenfunctions is the appearance of the combination βr, where β is an additional variational parameter independent of any quantum number, rather than the combination r/n which depends upon the particular state under consideration. The advantages of this choice are twofold. First the isolated hydrogen atom orbitals do not form a complete set without the inclusion of the continuum states.[15] Use of the set given by Eq. (1.12) has been shown to include contributions from these states.[16] Second, the virial theorem is automatically satisfied for any quantum mechanical system whose potential is a homogeneous function of the coordinates if a scale factor is introduced into the approximate wave function and varied so as to give the lowest energy.[17,14] The parameter β is such a scale factor and because its optimum value will be found, the properties of the states found with the approximate wave functions of Eq. (1.5) will be better than those which do not contain such a scaling.

Since the boundary surface was chosen to be a plane perpendicular to the z axis, there are no changes in the limits of integration over the variable ϕ. Consequently m remains a good quantum number. This means that we can separate the problem according to the m value of the particular level that we are interested in solving. Moreover, since the degeneracy of the two states $[n, l, \pm m]$ is not lifted we need consider only the positive m values. The original matrix equation given by Eq. (1.7) then reduces to a set of matrix equations for which $m = 0,1,2,\ldots$. That is

$$\mathbf{H}^{(m)}\mathbf{A}^{(m)} = E\mathbf{N}^{(m)}\mathbf{A}^{(m)}. \tag{1.13}$$

In the calculation of the matrix elements for these separate problems, the integration over the variable ϕ can now be replaced by multiplication with the factor $2\pi\delta_{m',m}$.

The calculation of the Hamiltonian matrix elements now proceeds as follows. Taking account of the truncation of the region of integration along with the above considerations the matrix elements can be written as

$$2\pi\left\{\int_0^R \int_0^\pi h^{(m)}_{n',l',nl} \sin\theta\, d\theta\, r^2\, dr + \int_R^\infty \int_{\cos^{-1}(R/r)}^\pi h^{(m)}_{n',l',nl} \sin\theta\, d\theta\, r^2\, dr\right\}, \tag{1.14}$$

where

$$h^{(m)}_{n'l',nl} \equiv \left[G^*(z)\phi^*_{n'l'm}(r,\beta)\right] H \left[G(z)\phi_{nlm}(r,\beta)\right].$$

It is here, in the lower limit of the θ integration of the second term, that the nonseparability of the problem becomes apparent with the appearance of the term $\cos^{-1}(R/r)$. For future convenience we shall denote this integration as

$$\int_T h^{(m)}_{n'l',nl}\, dV.$$

The matrix elements of the Hamiltonian are now expressible as

$$H^{(m)}_{n'l',nl} = \int_T (R - r\cos\theta)\phi_{n'l'm}(\mathbf{r},\beta) \times\{(R - r\cos\theta)[-\nabla^2 - (2/r)]\phi_{nlm}(\mathbf{r},\beta) - 2\hat{k}\cdot\nabla\phi_{nlm}(\mathbf{r},\beta)\}dV, \tag{1.15}$$

which simplifies upon using the relations

$$\left(-\nabla^2 - \frac{2}{r}\right)\phi_{nlm}(\mathbf{r},\beta) = \left\{-\beta^2 + \frac{2(\beta n - 1)}{r}\right\}\phi_{nlm}(\mathbf{r},\beta) \tag{1.16}$$

and

$$\hat{k}\cdot\nabla\phi_{nlm}(\mathbf{r},\beta) = \cos\theta\frac{\partial\phi_{nlm}}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\phi_{nlm}}{\partial\theta}. \tag{1.17}$$

The expression for the overlap matrix is given simply by

$$N^{(m)}_{n'l',nl}(R) = \int_T \{(R - r\cos\theta)^2\phi_{n'l'm}(\mathbf{r},\beta)\phi_{nlm}(\mathbf{r},\beta)\}dV. \tag{1.18}$$

The numerical solution of the matrix Eq. (1.13) is a two step process. Because of the complicated dependence of the matrices and the associated eigenvalues on the parameter β, it is impractical to develop the variational condition $\partial[E]/\partial\beta = 0$. Therefore, at a specific distance a value of β must be assumed and then the linear problem of Eq. (1.13) can be solved, yielding the eigenvalues and eigenvectors. At this point the value of β can be varied, the matrix elements calculated, and the matrix Eq. (1.13) is again solved. In this way one can search for the value of β that gives the best upper bound to the eigenvalue.

TABLE I. Convergence of the ground state energy for the hydrogen/impenetrable wall system at several distances. Distance is given in units of Bohr radii and energy is in units of Ry.

Matrix size \ R	0.0	0.2	0.8	4.0
3× 3	−0.2500	−0.2448	−0.4849	−0.9888
6× 6	−0.2500	−0.2735	−0.5012	−0.9955
10×10	−0.2500	−0.2786	−0.5042	−0.9969
15×15	···	−0.2800	−0.5058	−0.9972
21×21	···	−0.2801	−0.5064	−0.9973
28×28	···	−0.2802	−0.5065	−0.9974

Before the above procedure can be applied, it must first be decided to what extent the basis set of Eq. (1.12) will be extended in the expansion of the trial function. This determines the order of the matrix equation to be solved. Since only the positive m values, one at a time, need be considered the expansion of the trial function can be written as

$$\Psi_m(\mathbf{r}) = (R - r\cos)\sum_{j=1}^{N}\sum_{k=0}^{j-1} A^{(m)}_{j+k}\,\phi_{m+j,\,m+k,\,m}(\mathbf{r},\beta), \tag{1.19}$$

where m is fixed and $\phi_{n,l,m}(\mathbf{r},\beta)$ is the function given by Eq. (1.12). Once N is chosen, the size of basis set, and of the matrices $\mathbf{H}^{(m)}$ and $\mathbf{N}^{(m)}$, is easily seen to be $N(N+1)/2$. Increasing N is analogous to increasing the value of the principal quantum number n that is included in the expansion of

TABLE II. Ground state properties of the hydrogen/impenetrable wall system ($m = 0, p = 1$). Energies are in units of Ry, the dipole values $\bar{\mu}_z$ are given in units of $(ea_0/2)(= 1.271\ \text{D})$, and the distances are given in terms of Bohr radii ($a_0 = 0.529$ Å). $\bar{T}$ and $\bar{V}$ are the expectation values of the kinetic and potential energies, respectively.

R	β	E_0	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}$
0.0	1.000	−0.2500	···	0.2500	−0.2500
0.2	1.001	−0.2802	−6.383	0.3170	−0.5872
0.4	1.077	−0.3272	−5.099	0.4458	−0.7730
0.6	1.321	−0.4027	−3.735	0.6774	−1.0801
0.8	1.537	−0.5065	−2.617	0.9527	−1.4592
1.0	1.696	−0.6172	−1.877	1.1480	−1.7652
1.2	1.795	−0.7144	−1.407	1.2375	−1.9519
1.4	1.850	−0.7912	−1.092	1.2576	−2.0488
1.6	1.872	−0.8488	−0.865	1.2429	−2.0917
1.8	1.876	−0.8911	−0.693	1.2139	−2.1049
2.0	1.870	−0.9217	−0.559	1.1811	−2.1028
2.2	1.852	−0.9438	−0.451	1.1494	−2.0933
2.4	1.822	−0.9598	−0.364	1.1211	−2.0809
2.6	1.775	−0.9712	−0.292	1.0968	−2.0680
2.8	1.719	−0.9794	−0.234	1.0765	−2.0558
3.0	1.603	−0.9853	−0.186	1.0599	−2.0452
3.2	1.554	−0.9896	−0.147	1.0465	−2.0360
3.4	1.414	−0.9926	−0.116	1.0358	−2.0284
3.6	1.290	−0.9947	−0.091	1.0274	−2.0221
3.8	1.209	−0.9963	−0.071	1.0208	−2.0171
4.0	1.183	−0.9974	−0.055	1.0157	−2.0131
4.2	1.161	−0.9981	−0.042	1.0118	−2.0099
4.4	1.112	−0.9987	−0.032	1.0088	−2.0075
4.6	1.089	−0.9991	−0.024	1.0065	−2.0056

TABLE III. Properties of the first excited state of the hydrogen/impenetrable wall system ($m = 0, p = 2$). Units the same as in Table II.

R	β	$E(0,2)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}$
0.0	0.500	−0.1111	⋯	0.1111	−0.2222
0.2	0.506	−0.1198	−17.171	0.1300	−0.2498
0.4	0.636	−0.1321	−15.231	0.1623	−0.2944
0.6	0.728	−0.1493	−13.148	0.2074	−0.3568
0.8	0.793	−0.1687	−11.408	0.2436	−0.4123
1.0	0.848	−0.1856	−10.172	0.2610	−0.4466
1.2	0.855	−0.1988	−9.353	0.2669	−0.4657
1.4	0.865	−0.2087	−8.761	0.2694	−0.4781
1.6	0.866	−0.2164	−8.320	0.2702	−0.4866
1.8	0.868	−0.2224	−7.974	0.2704	−0.4928
2.0	0.869	−0.2272	−7.695	0.2700	−0.4972
2.2	0.866	−0.2311	−7.465	0.2693	−0.5004
2.4	0.863	−0.2342	−7.271	0.2684	−0.5027
2.6	0.858	−0.2369	−7.106	0.2674	−0.5042
2.8	0.853	−0.2390	−6.964	0.2662	−0.5052
3.0	0.849	−0.2408	−6.840	0.2651	−0.5058
3.2	0.843	−0.2423	−6.732	0.2639	−0.5061
3.4	0.840	−0.2435	−6.638	0.2627	−0.5062
3.6	0.835	−0.2446	−6.555	0.2616	−0.5061
3.8	0.829	−0.2454	−6.482	0.2605	−0.5059
4.0	0.823	−0.2462	−6.417	0.2595	−0.5056
4.2	0.819	−0.2468	−6.361	0.2585	−0.5053
4.4	0.813	−0.2473	−6.310	0.2576	−0.5049
4.6	0.808	−0.2477	−6.266	0.2568	−0.5045
4.8	0.800	−0.2481	−6.227	0.2561	−0.5041
5.0	0.793	−0.2484	−6.193	0.2554	−0.5038

TABLE V. Properties of the third excited state ($m = 0, p = 3$) of the hydrogen/impenetrable wall system. Note the discontinuity of the properties $\bar{\mu}_z$, $\bar{T}$, and $\bar{V}$ between the distances of 3.4–3.6a_0 which indicates a level crossing.

R	β	$E(0,3)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}$
0.0	0.268	−0.0625	⋯	0.0625	−0.1250
0.2	0.311	−0.0661	−32.516	0.0701	−0.1362
0.4	0.352	−0.0709	−30.202	0.0812	−0.1521
0.6	0.398	−0.0772	−27.665	0.0949	−0.1720
0.8	0.441	−0.0838	−25.323	0.1056	−0.1895
1.0	0.472	−0.0895	−23.551	0.1110	−0.2005
1.2	0.491	−0.0938	−22.314	0.1133	−0.2071
1.4	0.502	−0.0970	−21.444	0.1143	−0.2113
1.6	0.509	−0.0994	−20.804	0.1149	−0.2143
1.8	0.513	−0.1013	−20.317	0.1152	−0.2164
2.0	0.515	−0.1028	−19.932	0.1153	−0.2181
2.2	0.515	−0.1040	−19.623	0.1153	−0.2193
2.4	0.515	−0.1050	−19.365	0.1153	−0.2203
2.6	0.514	−0.1059	−19.151	0.1152	−0.2211
2.8	0.513	−0.1066	−18.968	0.1151	−0.2217
3.0	0.515	−0.1072	−18.809	0.1150	−0.2221
3.2	0.510	−0.1077	−18.676	0.1148	−0.2225
3.4	0.508	−0.1081	−18.558	0.1146	−0.2227
3.6	0.423	−0.1087	−5.856	0.2206	−0.3294
3.8	0.449	−0.1154	−4.709	0.2494	−0.3648
4.0	0.496	−0.1228	−3.590	0.2791	−0.4019
4.2	0.535	−0.1310	−2.568	0.3071	−0.4381
4.4	0.570	−0.1400	−1.663	0.3314	−0.4710
4.6	0.600	−0.1483	−0.876	0.3507	−0.4990
4.8	0.626	−0.1571	−0.199	0.3646	−0.5217
5.0	0.650	−0.1656	−0.383	0.3736	−0.5391

the trial function, but care has to be taken in this interpretation since the set of functions of Eq. (1.12) are not the isolated hydrogen atom wave functions.

The procedure of the calculation is now given by the following. First, the value of the m quantum number, which is still a good quantum number, is decided upon. Second, the eigenvalue's position in the ordered set

$$E_i^{(m)}(R) \quad i = 1,2,3,...$$

is chosen. This is done because the optimum value of β is dependent upon exactly which eigenvalue is to be minimized. Now the value of N of Eq. (1.19) is set and the optimum value of β and the associated eigenvalue at that matrix size are calculated. Next the value of N is increased by 1, which increases the matrix size by $N + 1$, and again the eigenvalue is minimized with respect to β. This process is repeated until the values of the minimized energy at two successive matrix sizes agree to a certain number of significant figures. In this report most of the results presented are calculated to four significant figures, recall that the energy is in units of Rydbergs, and this was obtained by going to matrix sizes of (28×28). An example of convergence of the ground state for several distances is given in Table I.

TABLE IV. Properties of the second excited state ($m = 1, p = 1$) of the hydrogen/impenetrable wall system. Units the same as in Table II.

R	β	$E(1,1)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}$
0.0	0.412	−0.1111	⋯	0.1111	−0.2222
0.2	0.449	−0.1150	−12.358	0.1190	−0.2340
0.4	0.486	−0.1192	−11.580	0.1282	−0.2474
0.6	0.519	−0.1239	−10.792	0.1387	−0.2626
0.8	0.559	−0.1291	−9.999	0.1507	−0.2798
1.0	0.590	−0.1347	−9.206	0.1643	−0.2991
1.2	0.625	−0.1409	−8.425	0.1794	−0.3203
1.4	0.656	−0.1476	−7.668	0.1956	−0.3431
1.6	0.687	−0.1545	−6.948	0.2121	−0.3667
1.8	0.713	−0.1619	−6.278	0.2282	−0.3900
2.0	0.738	−0.1693	−5.663	0.2430	−0.4123
2.2	0.759	−0.1766	−5.109	0.2561	−0.4327
2.4	0.779	−0.1837	−4.613	0.2671	−0.4508
2.6	0.796	−0.1905	−4.170	0.2758	−0.4663
2.8	0.811	−0.1968	−3.777	0.2824	−0.4792
3.0	0.822	−0.2027	−3.426	0.2871	−0.4898
3.2	0.831	−0.2081	−3.113	0.2901	−0.4982
3.4	0.838	−0.2129	−2.833	0.2918	−0.5047
3.6	0.845	−0.2173	−2.581	0.2923	−0.5097
3.8	0.848	−0.2213	−2.353	0.2920	−0.5133
4.0	0.851	−0.2248	−2.147	0.2911	−0.5159
4.2	0.852	−0.2279	−1.959	0.2896	−0.5175
4.4	0.853	−0.2307	−1.788	0.2878	−0.5185
4.6	0.853	−0.2331	−1.631	0.2858	−0.5189
4.8	0.851	−0.2353	−1.488	0.2837	−0.5190
5.0	0.849	−0.2372	−1.356	0.2815	−0.5187

The results of the calculation for the first four states are given in Tables II–V. There we have tabulated the optimum value of β and the energy for a range of distances of the proton from the plane. Also included are several properties of these states that shall be discussed later. In these tables we have labeled the states by their m-quantum number and their position in the spectrum of the reduced problem, that is the spectrum of levels having the same m value.

The results for the ground state energy can be compared to those obtained by Bruch and Ruijgrok.[4] These authors were mainly interested in the imaging system as a model of physical adsorption (see the next section); however the re-

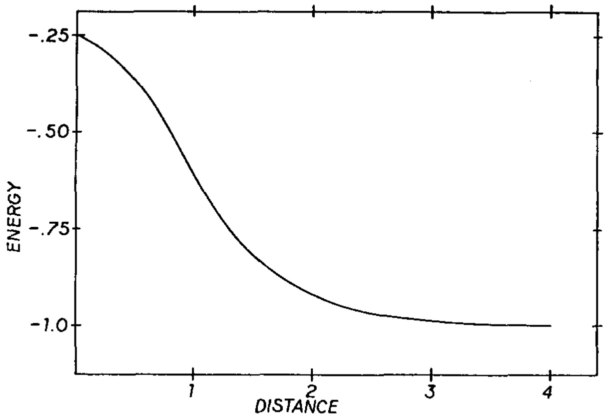

FIG. 2. Ground state energy as a function of distance of the hydrogen/impenetrable wall system. In this and the following figures energy is in units of Rydbergs and distance is in units of Bohr radii.

sults for a change of the boundary surface only are given for the ground state. Their approach to the problem is a variational one that is similar in spirit to the present one. The difference is that the problem is cast in confocal elliptic coordinates with the foci at the proton and the image proton. The trial function is then chosen as

$$\psi_t = \exp(-\alpha\xi/2)\sinh(\beta\eta/2)\sum_{k,l} C_{kl}\,\xi^k\eta^l. \tag{1.20}$$

In Eq. (1.20) ξ and η are the coordinates in the confocal elliptic system, α and β are nonlinear variational parameters, and the set C_{kl} constitutes the linear variational parameters. The important feature of the trial function (1.20) is that the boundary value of $\psi_t = 0$ on the plane is satisfied by the $\sinh(\beta\eta/2)$ term. After converting their results to Rydbergs, the two calculations agree to as many significant figures as are reported in that paper. For example, at a distance of 1.2 bohr radii from the plane, both methods yield a ground state energy of -0.7144 Ry.

However, results are given by Bruch and Ruijgrok only for the ground state so that there is no information on the manner in which the spectrum of a hydrogen atom changes as an infinite plane potential moves in from infinity. This information is easier to interpret when it is presented as a graph showing the energy as a function of the distance of the proton from the plane. These graphs are presented in Figs. 2 and 3.

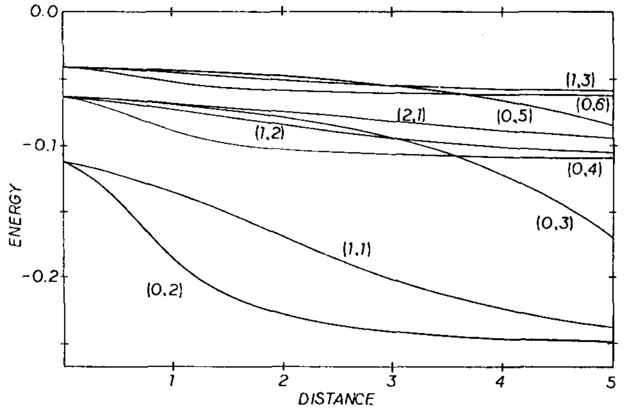

FIG. 3. The first 13 excited states of the hydrogen/impenetrable wall system.

It is evident from Fig. 2 that when the proton is located 4 Bohr radii away from the plane there is very little change in the ground state energy. As the distance from the plane decreases, the energy increases until, at $R = 0$, it is equal to -0.25 Ry. This result is the expected one since when the proton is located on the plane the Hamiltonian is separable and the problem is exactly solvable. The solutions are the isolated hydrogen atom eigenfunctions restricted by the selection rule

$$|l - m| = \text{odd}. \tag{1.21}$$

This result was first pointed out by Levine,[5] who noted its importance for the problem of a shallow donor impurity located at the surface of a semiconductor (see paper II in this series).[11]

The correct values at the $R = 0$ limit are also obtained for the excited states in Fig. 3. In that figure the states are labeled by their m value and their position in the matrix by the notation (m, p). There are several interesting features exhibited by the spectrum presented in Fig. 3. At $R = \infty$ there exist two states with $n = 2$ and $m = 0$, i.e., the $2s$ and $2p_0$ states. However, at $R = 0$ there exists only one state with $n = 3$ and $m = 0$ because of the selection rule (1.21) and that is the $3p_0$ state. Therefore one of the states with $n = 2$, $m = 0$ at $R = \infty$ must map onto a state with $n = 4$ at $R = 0$. At $R = 5a_0$ the state which does this is labeled by (0,3). As R decreases, the energy of state (0,3) increases until it crosses the state (0,4). These two states possess the same azimuthal quantum number m and are therefore eigenvalues of the same reduced matrix problem. This appears to be a true crossing for two reasons. First, the eigenvalues become equal, to four figure accuracy which is the limit of accuracy in the present calculations, at a distance from the plane of approximately $3.58a_0$. Second, the properties derived from the wave functions of these two states have a consistent interpretation only if such a crossing takes place. That is, the dipole in the z direction, the average kinetic energy and the average potential energy should be continuous functions of the distance from the plane and this would not be the case if such a crossing did not occur. As the distance to the plane is decreased even further another crossing occurs. However, this crossing is for states of differing azimuthal symmetry so there is no reason to suspect another symmetry of the system at this distance.

The ground state of an isolated hydrogen atom does not possess a net dipole moment. However when the charge distribution is changed by the presence of the boundary plane this is no longer true. Because of the azimuthal symmetry, the dipole moment of the ground state will be in the z direction and the dipole moment operator can be written as[4]

$$\mu_z \equiv z = r\cos\theta. \tag{1.22}$$

A positive dipole moment is directed away from the boundary plane. The convention used here is that the dipole points from the negative to the positive charge.

The manner in which the average value of μ is calculates is modified slightly due to the nonorthogonality previously discussed. First the matrix $\mathbf{D}^{(m)}$ is calculated, where

$$(\mathbf{D}^{(m)})_{n'l',nl} = \int_T \phi_{n'l'm}\,\mu\phi_{nlm}\,dV \tag{1.23}$$

and the optimized value of β is used. The expectation value of μ for a state labeled by (m, k) is then given by

$$\bar{\mu}_k^{(m)} = \frac{\mathbf{A}_k^{(m)*}\mathbf{D}^{(m)}\mathbf{A}_k^{(m)}}{\mathbf{A}_k^{(m)*}\mathbf{N}^{(m)}\mathbf{A}_k^{(m)}}, \tag{1.24}$$

where $\mathbf{A}_k^{(m)}$ is the optimized k th eigenvector of Eq. (1.13) and $\mathbf{N}^{(m)}$ is the overlap matrix. The dipole expectation values are given in Tables II–V. As expected the influence of the boundary plane is to push the electronic charge distribution away so that its "center of gravity" lies behind the proton and yields negative $\bar{\mu}$. Note also that the dipole moments fall off much less rapidly as a function of R for the excited states. This is due to the fact that the excited states, because of their greater spatial extent, "feel" the presence of the plane for a further distance than does the ground state.

The average kinetic and potential energies can be calculated in a manner similar to that for the dipole. But now it is not necessary to calculate any additional matrices, for $\mathbf{T}^{(m)}$ and $\mathbf{V}^{(m)}$ are already available from the calculation of $\mathbf{H}^{(m)}$. These expectation values have also been computed and are given in Tables II–V.

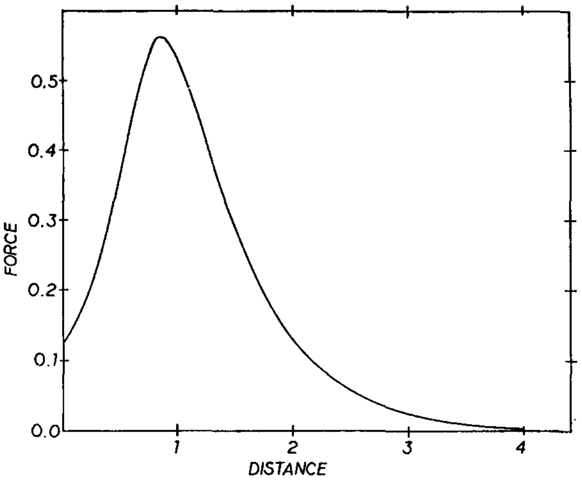

FIG. 4. Force on the proton when the electron is in its ground state.

In examining the expectation values of the kinetic and potential energies of the electron given in these tables it is apparent that the relation

$$2\bar{T} = -\bar{V} \tag{1.25}$$

is no longer satisfied. Equation (1.25) is of course the statement of the virial theorem for an isolated system with a Coulomb interaction. When the system depends upon a parameter which is assumed to be fixed, which for example can be the internuclear coordinates of a diatomic molecule in the Born–Oppenheimer approximation or the distance to the

TABLE VI. Ground state properties of the hydrogen/perfectly imaging substrate system. $\bar{V}_1$, $\bar{V}_2$, and $\bar{V}_3$ denote the average values of the last three interaction terms in the Hamiltonian of Eq. (2.1). $\bar{T}$ and $\bar{V}$ are the expectation values of the kinetic and potential energies, respectively.

R	β	$E(0, 1)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_3$
0.2	0.174	−0.0633	−11.408	0.0673	−0.1470	−0.1267	0.1440
0.4	0.399	−0.0726	−9.597	0.1055	−0.2995	−0.1450	0.2664
0.6	0.753	−0.1039	−6.482	0.2578	−0.5789	−0.2002	0.4174
0.8	1.142	−0.1839	−3.671	0.6107	−1.0821	−0.2841	0.5717
1.0	1.439	−0.3049	−2.237	0.9413	−1.5444	−0.3326	0.6308
1.2	1.621	−0.4274	−1.532	1.1139	−1.8209	−0.3409	0.6205
1.4	1.725	−0.5309	−1.125	1.1758	−1.9612	−0.3295	0.5848
1.6	1.780	−0.6123	−0.856	1.1821	−2.0270	−0.3105	0.5430
1.8	1.806	−0.6748	−0.662	1.1641	−2.0518	−0.2893	0.5024
2.0	1.813	−0.7224	−0.514	1.1376	−2.0564	−0.2684	0.4648
2.2	1.794	−0.7589	−0.398	1.1098	−2.0511	−0.2486	0.4311
2.4	1.751	−0.7870	−0.305	1.0843	−2.0419	−0.2304	0.4009
2.6	1.690	−0.8090	−0.231	1.0623	−2.0316	−0.2139	0.3741
2.8	1.616	−0.8265	−0.172	1.0441	−2.0219	−0.1988	0.3502
3.0	1.539	−0.8405	−0.125	1.0296	−2.0135	−0.1853	0.3287
3.2	1.466	−0.8519	−0.088	1.0183	−2.007	−0.1731	0.3095
3.4	1.398	−0.8614	−0.059	1.0097	−2.001	−0.1621	0.2923
3.6	1.336	−0.8695	−0.037	1.0034	−1.9974	−0.1522	0.2766
3.8	1.280	−0.8764	−0.021	0.9989	−1.9946	−0.1433	0.2625
4.0	1.228	−0.8825	−0.009	0.9959	−1.9927	−0.1353	0.2497
4.2	1.182	−0.8878	−0.0004	0.9939	−1.9916	−0.1281	0.2380
4.4	1.140	−0.8926	0.005	0.9928	−1.9911	−0.1216	0.2273
4.6	1.100	−0.8969	0.009	0.9922	−1.991	−0.1156	0.2174
4.8	1.065	−0.9009	0.012	0.9920	−1.9912	−0.1102	0.2084
5.0	1.033	−0.9046	0.013	0.9922	−1.9915	−0.1053	0.2001
5.2	1.003	−0.9079	0.013	0.9925	−1.9920	−0.1008	0.1924
5.4	0.977	−0.9111	0.013	0.9929	−1.9925	−0.0967	0.1853
5.6	0.951	−0.9140	0.012	0.9934	−1.9931	−0.0929	0.1787
5.8	0.931	−0.9168	0.012	0.9939	−1.9937	−0.0894	0.1725
6.0	0.912	−0.9193	0.011	0.9943	−1.9992	−0.0862	0.1668

plane in the present problem, the virial theorem must be modified from the form given in Eq. (1.25). This is due to the fact that the quantity known as the "virial"

$$-1/2 \sum_i \overline{r_i F_i}$$

must include *all* of the forces acting on the system. This means that since the proton is assumed to be in a fixed position some external force must be acting on it so that it remains stationary. When this external force is taken into account the correct form of the virial theorem is given by

$$2\overline{T} = -\overline{V} - R\,\frac{\partial E}{\partial R}. \qquad (1.26)$$

The force acting on the proton is therefore given by the quantity $\partial E/\partial R$. Note that in the present case the Hellman–Feynman theorem is no longer valid.[4,18] That is

$$\frac{\partial E}{\partial R} \neq \left\langle \frac{\partial H}{\partial R} \right\rangle$$

because the region of integration of the matrix elements is dependent upon R. This points out the importance of the virial theorem, and the choice of the basis set, if the force on the proton is to be found.

The results presented in Table II have been used, with the aid of Eq. (1.26), to calculate the force on the proton when the atom is in its ground state, as a function of distance. This force is presented graphically in Fig. 4. The interesting features of this force are that it has a maximum at approximately $0.9a_0$ and that it is nonzero at $R = 0$. At $R = \infty$ the force is zero and at $R = -\infty$ is must also be zero for then the electron and proton have been completely separated. Therefore a maximum must exist between these two limits.

II. IMAGE CHARGES AND A MODEL OF PHYSISORPTION OF ATOMIC HYDROGEN

When a gas adsorbs onto a solid surface, depending upon the magnitude of the binding energy, it is commonly said to be chemisorbed or physically adsorbed. The binding energy that is ascribed to chemical adsorption can be several electron volts while that of physisorption is of the order of a fraction of an electron-volt. The difference in binding energy magnitudes is a reflection of the different processes which are believed to occur in the two types of adsorption; in chemical adsorption a bond is formed between the adsorbed molecule or atom and the surface while in physical adsorption significant charge rearrangement associated with bond formation is absent.

Physical adsorption is usually thought to be due to a potential that is made up of an attractive long-range van der Waals (or dispersion) potential and a short-range repulsive potential due to the overlap of the electrons of the adatom

TABLE VII. Properties of the first excited state ($m = 1, p = 1$), the $2p$, $|m| = 1$ doubly degenerate state, of the hydrogen/perfectly imaging substrate system.

R	β	$E(1, 1)$	$\bar{\mu}_z$	$\overline{T}$	$\overline{V}_1$	$\overline{V}_2$	$\overline{V}_3$
0.2	0.149	− 0.0602	− 11.906	0.0606	− 0.0506	− 0.1207	0.0505
0.4	0.150	− 0.0604	− 11.486	0.0609	− 0.0530	− 0.1210	0.0527
0.6	0.152	− 0.0605	− 11.059	0.0614	− 0.0565	− 0.1213	0.0558
0.8	0.156	− 0.0608	− 10.624	0.0621	− 0.0620	− 0.1217	0.0608
1.0	0.162	− 0.0611	− 10.170	0.0636	− 0.0717	− 0.1223	0.0694
1.2	0.177	− 0.0617	− 9.676	0.0671	− 0.0915	− 0.1234	0.0860
1.4	0.216	− 0.0630	− 9.077	0.0759	− 0.1287	− 0.1253	0.1152
1.6	0.286	− 0.0656	− 8.299	0.0920	− 0.1766	− 0.1288	0.1478
1.8	0.363	− 0.0697	− 7.407	0.1133	− 0.2234	− 0.1335	0.1740
2.0	0.434	− 0.0752	− 6.503	0.1372	− 0.2675	− 0.1386	0.1936
2.2	0.496	− 0.081	− 5.656	0.1615	− 0.3079	− 0.1431	0.2070
2.4	0.548	− 0.089	− 4.902	0.1840	− 0.3437	− 0.1465	0.2167
2.6	0.593	− 0.0976	− 4.248	0.2036	− 0.3744	− 0.1486	0.2218
2.8	0.630	− 0.1058	− 3.688	0.2196	− 0.3998	− 0.1494	0.2238
3.0	0.660	− 0.1138	− 3.207	0.2322	− 0.4205	− 0.1490	0.2235
3.2	0.685	− 0.1215	− 2.792	0.2416	− 0.4369	− 0.1477	0.2215
3.4	0.705	− 0.1288	− 2.432	0.2484	− 0.4499	− 0.1457	0.2183
3.6	0.722	− 0.1356	− 2.115	0.2531	− 0.4599	− 0.1431	0.2143
3.8	0.735	− 0.1419	− 1.836	0.2559	− 0.4675	− 0.1401	0.2098
4.0	0.745	− 0.1476	− 1.587	0.2575	− 0.4732	− 0.1369	0.2050
4.2	0.753	− 0.1529	− 1.364	0.2580	− 0.4774	− 0.1334	0.2000
4.4	0.757	− 0.1576	− 1.163	0.2578	− 0.4804	− 0.1299	0.1949
4.6	0.760	− 0.162	− 0.982	0.2570	− 0.4825	− 0.1263	0.1899
4.8	0.760	− 0.1659	− 0.818	0.2558	− 0.4839	− 0.1227	0.1848
5.0	0.757	− 0.1695	− 0.669	0.2544	− 0.4847	− 0.1191	0.1799
5.2	0.753	− 0.1727	− 0.535	0.2528	− 0.4852	− 0.1155	0.1751
5.4	0.747	− 0.1757	− 0.413	0.2511	− 0.4853	− 0.112	0.1705
5.6	0.739	− 0.1783	− 0.303	0.2495	− 0.4853	− 0.1085	0.1660
5.8	0.731	− 0.1808	− 0.204	0.2479	− 0.4851	− 0.1051	0.1616
6.0	0.722	− 0.1830	− 0.116	0.2463	− 0.4848	− 0.1019	0.1574
6.2	0.711	− 0.1850	− 0.036	0.2449	− 0.4845	− 0.0987	0.1533
6.4	0.700	− 0.1868	− 0.034	0.2436	− 0.4842	− 0.0956	0.1494
6.6	0.689	− 0.1885	− 0.096	0.2424	− 0.4839	− 0.0925	0.1456

with those of the metal. The problem is a many electron one and has been the subject of much recent work.[19–22,24] However, in the case of atomic hydrogen an idealized model can be constructed, as presented by Bruch and Ruijgrok,[4] which reduces to a one electron problem.

The model consists of replacing the metal by a perfectly imaging medium with instantaneous Coulomb interactions. The effect of the exchange repulsion is modeled by the condition that the atomic electron is excluded from the metal (i.e., its wave function vanishes on the surface) resulting in a repulsive (positive) contribution to the total electronic energy due to raising of the electron kinetic energy. As such, the use of the "surface boundary condition model" yields an upper bound to the exchange-repulsion contribution to the total electronic energy. The potential that the proton then experiences, called by Bruch and Ruijgrok the "holding potential," is given by the change in the ground state electronic energy plus the interaction of the proton with his image in the metal.

Solving the problem of the ground state electronic energy of this system is the first step in obtaining the holding potential of the atomic hydrogen. Taking into account the possibility of a finite dielectric constant for region B of Fig. 1, the Hamiltonian for the electron can be written as

$$H = \frac{-h^2}{2m}\nabla^2 - \frac{e^2}{r} + \frac{(\epsilon-1)}{(\epsilon+1)}\frac{e^2}{[r^2+4R^2-4rR\cos\theta]^{1/2}} - \frac{(\epsilon-1)}{4(\epsilon+1)}\frac{e^2}{(R-r\cos\theta)}. \tag{2.1}$$

Equation (1.3) must, of course, be solved subject to the boundary condition that $\psi = 0$ on the surface $z = R$. The coordinate system of Eq. (2.1) is that indicated in Fig. 1 and ϵ denotes the static dielectric constant of region B. We shall be interested mainly in the "metallic" limit, i.e., $\epsilon \to \infty$. The last two terms in Eq. (2.1) are, respectively, the interaction of the electron with the image of the proton and the interaction of the electron with its own image, and hence the extra factor of 1/2 (energy of assembly).

The calculation of the energy eigenvalues and properties of these states proceeds exactly as previously outlined. Now, however, there are two additional matrix elements to be included in the matrix equations. The electron-image electron term is not hard to calculate analytically but this is

TABLE VIII. Properties of the second excited state, originating from the 2*s*, $m = 0$ state, of the hydrogen/perfectly imaging substrate system.

R	β	$E(0,2)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_3$
0.2	0.135	− 0.0590	− 12.162	0.0615	− 0.0773	− 0.1184	0.0756
0.4	0.144	− 0.0602	− 11.526	0.0622	− 0.0590	− 0.1207	0.0573
0.6	0.154	− 0.0608	− 11.052	0.0630	− 0.0623	− 0.1219	0.0604
0.8	0.191	− 0.0616	− 10.669	0.0663	− 0.0836	− 0.1229	0.0786
1.0	0.423	− 0.0656	− 10.648	0.0983	− 0.2011	− 0.1213	0.1586
1.2	0.537	− 0.0733	− 10.036	0.1239	− 0.2692	− 0.1207	0.1927
1.4	0.596	− 0.0819	− 9.344	0.1430	− 0.3128	− 0.1207	0.2086
1.6	0.635	− 0.0906	− 8.736	0.1587	− 0.3451	− 0.1203	0.2161
1.8	0.662	− 0.0989	− 8.228	0.1716	− 0.3700	− 0.1193	0.2187
2.0	0.681	− 0.1068	− 7.806	0.3897	− 0.3897	− 0.1176	0.2183
3.0	0.727	− 0.1378	− 6.508	0.2119	− 0.4430	− 0.1045	0.1977
4.0	0.720	− 0.1580	− 5.885	0.2230	− 0.4631	− 0.0899	0.1720
5.0	0.678	− 0.1716	− 5.497	0.2291	− 0.4730	− 0.0779	0.1501
6.0	0.609	− 0.1818	− 4.762	0.2368	− 0.4806	− 0.0722	0.1343
2.2	0.695	− 0.1141	− 7.454	0.1909	− 0.4053	− 0.1155	0.2159
2.4	0.707	− 0.1208	− 7.157	0.1979	− 0.4179	− 0.1130	0.2122
2.6	0.716	− 0.127	− 6.907	0.2036	− 0.4280	− 0.1103	0.2078
2.8	0.722	− 0.1326	− 6.692	0.2082	− 0.4363	− 0.1070	0.2028
3.0	0.727	− 0.1378	− 6.508	0.2119	− 0.4430	− 0.1045	0.1977
3.2	0.729	− 0.1425	− 6.348	0.2150	− 0.4485	− 0.1015	0.1925
3.4	0.729	− 0.1469	− 6.209	0.2175	− 0.4531	− 0.0985	0.1872
3.6	0.728	− 0.1509	− 6.088	0.2197	− 0.4570	− 0.0956	0.1820
3.8	0.726	− 0.1546	− 5.980	0.2215	− 0.4603	− 0.0927	0.1770
4.0	0.720	− 0.158	− 5.885	0.2230	− 0.4631	− 0.0899	0.1720
4.2	0.714	− 0.1611	− 5.799	0.2244	− 0.4655	− 0.0873	0.1673
4.4	0.706	− 0.1640	− 5.720	0.2257	− 0.4677	− 0.0847	0.1627
4.6	0.698	− 0.1667	− 5.646	0.2264	− 0.4696	− 0.0823	0.1583
4.8	0.689	− 0.1692	− 5.573	0.2280	− 0.4714	− 0.0800	0.1541
5.0	0.678	− 0.1716	− 5.497	0.2291	− 0.4730	− 0.0779	0.1501
5.2	0.667	− 0.1739	− 5.414	0.2303	− 0.4745	− 0.0760	0.1464
5.4	0.654	− 0.1760	− 5.316	0.2315	− 0.4760	− 0.0744	0.1429
5.6	0.642	− 0.1780	− 5.192	0.2329	− 0.4870	− 0.0731	0.1396
5.8	0.625	− 0.1800	− 5.020	0.2346	− 0.4789	− 0.0723	0.1367
6.0	0.609	− 0.1810	− 4.762	0.2368	− 0.4806	− 0.0722	0.1343

TABLE IX. Properties of the third excited state originating from the $2p$, $m = 0$ state, of the hydrogen/perfectly imaging substrate system.

R	β	$E(0, 3)$	$\bar{\mu}_z$	$\bar{T}$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_3$
0.2	0.119	−0.0524	−14.060	0.0553	−0.0772	−0.1058	0.0753
0.4	0.125	−0.0541	−13.102	0.0581	−0.0676	−0.1092	0.0646
0.6	0.131	−0.0552	−12.395	0.0594	−0.0655	−0.1112	0.0621
0.8	0.141	−0.0562	−11.746	0.0615	−0.0707	−0.1131	0.0659
1.0	0.159	−0.0574	−11.163	0.0645	−0.0773	−0.1144	0.0698
1.2	0.176	−0.0586	−10.495	0.0656	−0.0728	−0.1162	0.0648
1.4	0.182	−0.0595	−9.870	0.0649	−0.0665	−0.1179	0.0601
1.6	0.185	−0.0600	−9.354	0.0645	−0.0653	−0.1189	0.0596
1.8	0.189	−0.0605	−8.898	0.0647	−0.0669	−0.1195	0.0612
2.0	0.197	−0.0609	−8.469	0.0654	−0.0710	−0.1198	0.0645
2.2	0.209	−0.0614	−8.065	0.0666	−0.0772	−0.1199	0.0691
2.4	0.221	−0.0619	−7.684	0.0682	−0.0845	−0.1198	0.0742
2.6	0.238	−0.0625	−7.317	0.0706	−0.0938	−0.1194	0.0815
2.8	0.254	−0.0632	−6.952	0.0737	−0.1039	−0.1190	0.0860
3.0	0.270	−0.0640	−6.574	0.0779	−0.1153	−0.1187	0.0921
3.2	0.283	−0.0651	−6.158	0.0840	−0.1289	−0.1187	0.0985
3.4	0.299	−0.0665	−5.665	0.0948	−0.1489	−0.1196	0.1072
3.6	0.317	−0.0686	−5.027	0.1165	−0.1830	−0.1229	0.1207
3.8	0.342	−0.0722	−4.183	0.1596	−0.2432	−0.1305	0.1420
4.0	0.378	−0.0781	−3.197	0.2198	−0.3216	−0.1419	0.1657
4.2	0.427	−0.0862	−2.197	0.2745	−0.3907	−0.1526	0.1825
4.4	0.482	−0.0957	−1.271	0.3149	−0.4424	−0.1603	0.1921
4.6	0.532	−0.1059	−0.466	0.3421	−0.4797	−0.1651	0.1969
4.8	0.576	−0.1161	−0.211	0.3589	−0.5060	−0.1675	0.1985
5.0	0.610	−0.1260	0.773	0.3677	−0.5238	−0.1680	0.1981
5.2	0.635	−0.1354	1.236	0.3705	−0.5352	−0.1670	0.1963
5.4	0.652	−0.1441	1.611	0.3690	−0.5918	−0.1648	0.1935
5.6	0.663	−0.1521	1.901	0.3644	−0.5448	−0.1616	0.1899
5.8	0.667	−0.1593	2.097	0.3576	−0.5452	−0.1575	0.1858
6.0	0.669	−0.1658	2.169	0.3489	−0.5435	−0.1523	0.1811
6.2	0.667	−0.1715	2.047	0.3384	−0.5400	−0.1455	0.1756
6.4	0.667	−0.1765	1.575	0.3255	−0.5346	−0.1360	0.1686
6.6	0.669	−0.1808	0.455	0.3083	−0.5264	−0.1215	0.1588

not true of the electron-image proton interaction given by the third term of Eq. (2.1). Because of the law of cosines denominator and the restricted region of integration given by Eq. (1.14), it has not been possible to find a closed form expression for that matrix element.

There are two ways of calculating the electron-image proton matrix element. One can either use a numerical approach or, by expanding the denominator of the electron-image proton potential in the standard series of Legendre polynomials, integrate term by term. The former method was chosen because the expressions and summation of the latter method consumed a much greater amount of computer time than a straightforward numerical integration of the matrix elements by the Gauss–Legendre and Gauss–Laguerre methods.

The results of this calculation are given in Tables VI–IX for the first five states. (Recall that $m \neq 0$ states are doubly degenerate.) The ground state of this system is shown graphically in Fig. 5 where the ground state of the nonimaging case has been repeated for comparison. As is apparent from this figure and shown explicitly in Table VI where all the energy contributions are tabulated, the interaction of the electron with the image of the proton, which is repulsive, dominates the electron-image electron interaction which is attractive. In this instance also the $R = 0$ value is an expected one. When $R = 0$, and the system is perfectly imaging, the proton and image proton charges cancel each other (as far as the electron is concerned) and the problem is now that of an electron bound by its image, which is an exactly solvable[23,24] one-dimensional Coulomb problem, yielding a ground state energy of − 0.0625 Ry.

The first excited state of the isolated atom (principal quantum number $n = 2$) is fourfold degenerate. In the pres-

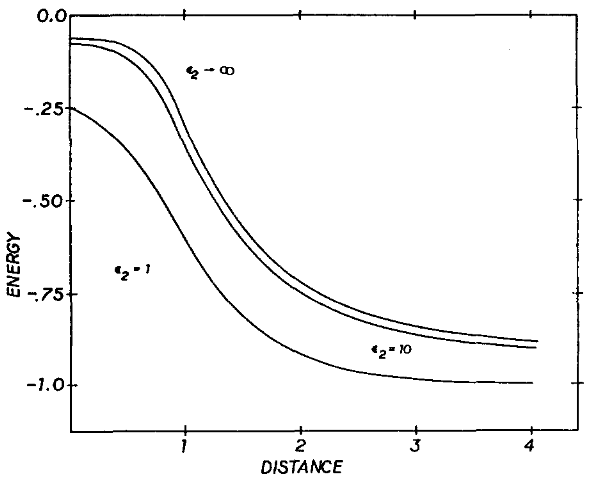

FIG. 5. Ground state energy as a function of proton distance from the plane for the perfectly imaging substrate ($\epsilon_2 \to \infty$) system.

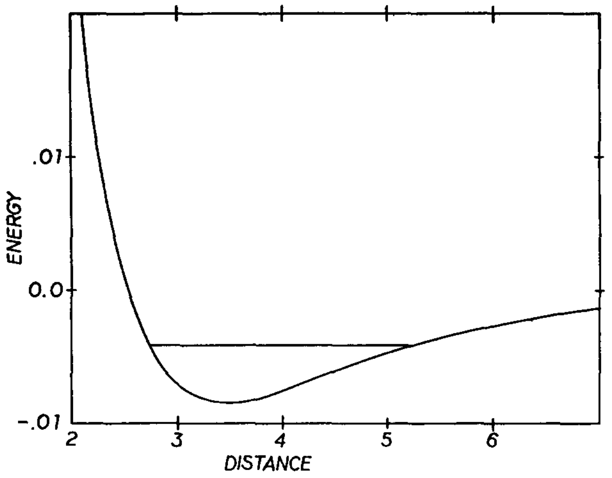

FIG. 6. The holding potential of Bruch and Ruijgiok in which the image electron–proton interaction has not been included.

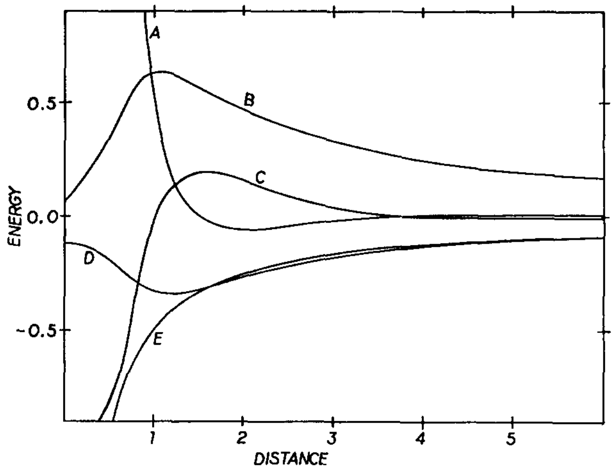

FIG. 7. The various contributions to the interaction potential. The curve A represents the change in the expectation value of the electron–proton interaction from its value for the isolated hydrogen atom. Curve B is the average value of the electron-image proton interaction ($\overline{Ve}$-imp). Curve C is the change in the electron's average kinetic energy. Curve D represents the average value of the electron-image electron interaction ($\overline{Ve}$-ime). Curve E is the proton-image proton interaction ($-1/2R$).

ence of the metal this degeneracy is partially lifted, i.e., while the $2p$, $|m| = \pm 1$ states are still degenerate (due to polar angle symmetry around the normal to the metal plane), the $2s$ and $2p$, $m = 0$ states mix and their energy split. The energy as a function of distance of the proton from the surface for the $2p$, $|m| = 1$ doubly degenerate state is given in Table VII, and those for the states originating from the $2s$ and $2p$, $m = 0$ in Tables VIII and IX, respectively. These results are in good agreement with those given in Table III of Ref. 4 (to convert to the values of Ref. 4 substract from our energies the proton-image proton interaction $-1/2R$ and divide the result by two to convert to atomic units).

Having solved the electronic part of the problems it is possible to construct the holding potential of the atomic hydrogen. The potential that the proton experiences has two contributions. First, still in the Born–Oppenheimer approximation, is the change in the electronic energy of the system as a function of distance. The second is the proton-image proton interaction which is attractive in nature.

Calculating the holding potential for the ground state of the system [i.e., using the energy values in Table VI, subtracting from them the ground state energy at infinite separation (-1.0 Ry)] and adding the proton-image proton interaction energy ($-1/(2R)$ Ry)] yields the potential curve shown in Fig. 6, which exhibits a potential well of depth

$$8.6\times 10^{-3}\ \text{Ry at } R = 3.44a_0$$

in agreement with Ref. 4 (see in particular Sec. 9.1). The various contributions to this holding potential are shown in Fig. 7. The ground state expectation values of the kinetic energy and electron–proton interaction, from which the corresponding energies at $R = \infty$ have been subtracted are shown as curves C and A, respectively. The electron-image proton and electron-image electron interactions are denoted as curves B and D, respectively. The proton-image proton energy, given by $-1/(2R)$ Ry, is denoted as curve E. The sum of the curves in Fig. 7 yields the holding potential curve given in Fig. 6.

Finally we comment on the dipole expectation values given in Tables VI–IX. As shown in Table VI for the ground state the dipole moment is negative, i.e., directed inward, for locations of proton near and beyond the minimum in the holding potentials (same as found in Ref. 4), changing sign of the vicinity of $R = 4.1a_0$. The values of the dipole moment are much larger for the excited states and fall off slower as the atom is removed from the surface reflecting the larger spatial extent of the excited states wave functions. It is of interest to note that for the distances included in the tables the dipole of the $2s$, $m = 0$ state remains negative and large even up to $\sim 7.0\mathrm{a}_0$, while for the $2p$, $m = 0$ it changes orientation between $R = 5.0$ and $5.2a_0$ and past that distance an oscillation in magnitude is observed. Similarly a reversal of sign occurs for the $2p, m = 1$ (doubly degenerate) state between $R = 6.4$ and $6.6a_0$. It has been suggested[21] that the quantitative balance between contributions which determine the orientation of dipoles of physisorbed atoms may differ in light and heavy atoms, and this may be a demonstration of such an effect.[4]

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