Hydrogenic System in Half Space

S. H. Patil

Department of Physics, Indian Institute of Technology Bombay 400 076, India

Reprint requests to Dr. S. H. P.; E-mail: sharad@phy.iitb.ac.in

Z. Naturforsch. **59a,** 455 – 466 (2004); received April 8, 2004

Some structural properties of the energy eigenfunctions of a hydrogenic system in half space, are analysed. Specifically, we have obtained the asymptotic behaviour when the electron is far away from the nucleus, the coalescence property when it is close to the nucleus, the inflection property when it is close to the potential barrier, the property when the nucleus is far away from the barrier, and a virial relation. Simple model wave functions are developed, incorporating these properties which give accurate values for the energies and some other physical quantities, and give a useful understanding of the physical structure of the system.

Key words: Hydrogenic System; Half Space.

1. Introduction

The hydrogenic system in half space is of considerable interest. It provides a useful model for the description of surface physics. In particular, it has been used to describe an electron moving in the potential of a heavy hole near a semi-conductor surface [1], and to describe the surface effects on impurity states near the boundary of a crystal or semi-conductor surface [2]. In these cases the potential is Coulombic inside the solid but shoots up to infinity at the boundary. The model has been extended to describe the effect of the surface depth on impurity states in semiconductors [3], and to a hydrogen atom interacting with an impenetrable surface of polar crystals [4], for which the potential is Coulombic with some additions in the free space but shoots up to infinity at the crystal surface. The main feature of the model is, that the Schrödinger equation for the hydrogenic system in half space is separable in terms of what are known as confocal elliptic coordinates or prolate spheroidal coordinates [1, 2]. With these coordinates, the problem has been investigated with different approaches, using infinite continued fractions [1], truncated matrix equations [2, 5, 6], Killingbeck-Miller method [7], and an eigenfunction expansion [8]. These approaches have yielded accurate, numerical values for the energy eigenvalues and eigenfunctions. The topic is of general interest and has been included in the review by Jaskolski [9]. However, what is lacking is a description in terms of simple model wave functions, and an analysis of the structural properties of the eigenstates in different domains. An understanding of these properties is very helpful in the developing of model wave functions which are compact and accurate, and which provide a useful insight into the physical structure of the system.

Here, we analyse the structural properties of the hydrogenic system in half space, the asymptotic behaviour when the electron is far away from the nucleus, the coalescence property when the electron is close to the nucleus, and the inflection property when the electron is close the potential barrier. We also describe the virial relation and the structure of the wave function when the nucleus is far away from the potential barrier. We then develop some simple model wave functions for some states, incorporating these properties. These wave functions not only provide accurate values for the energies and some other physical properties, but also provide a very useful insight into their physical structure. We also obtain a simple, perturbative expression for the energy when the nucleus is close to the surface. Finally, we consider the scaling property and obtain an estimation for the spectrum of helium in half space. Atomic units $e = m = \hbar = 1$ are used throughout.

2. Some General Properties

The hydrogenic system in the half space $-\infty < x < \infty$, $-\infty < y < \infty$, and $z \geq 0$, with the nucleus at

$(0,0,R/2)$, is described by the potential

$$V(x,y,z) = -\frac{Z}{[x^2+y^2+(z-R/2)^2]^{1/2}} \quad \text{for } z \geq 0,$$
$$= \infty \qquad \text{for } z < 0, \tag{2.1}$$

where Z is the nuclear charge, which is 1 for the hydrogen atom. The potential being infinite for $z<0$ implies that the wave function vanishes at $z=0$, and the energy eigenfunctions are not separable in terms of spherical coordinates. Elliptic coordinates are appropriate [1, 2] for this case, and we begin by describing some general properties of the hydrogenic system in half space, in terms of elliptic coordinates. With the foci of the ellipse at $(0,0,R/2)$ and $(0,0,-R/2)$, the elliptic coordinates u,v,ϕ are

$$u = \frac{r_1+r_2}{R}, \quad v = \frac{r_1-r_2}{R}, \quad \phi, \tag{2.2}$$
$$r_1 = |\boldsymbol{r} - \frac{1}{2}\boldsymbol{R}|, \quad r_2 = |\boldsymbol{r} + \frac{1}{2}\boldsymbol{R}|,$$

where $\boldsymbol{r}$ describes the vectorial position of the electron from the centre, and $\boldsymbol{R} = R\boldsymbol{k}$ with $\boldsymbol{k}$ being a unit vector in the z direction. It is noted that $z \geq 0$ corresponds to $v \leq 0$.

2.1. Schrödinger Equation

For the hydrogen atom in half space we take the potential to be

$$V = -\frac{Z}{r_1} + \frac{1}{u^2-v^2}V_0\theta(v), \tag{2.3}$$

where V_0 is a large positive quantity which we ultimately take to the limit of infinity, and $\theta(v)$ is the Heaviside step function. The first term in this potential is the Coulombic term, and the second term is the infinite barrier which confines the electron to negative values of v or equivalently positive values of z. The second term is taken in this form to allow separability of the Schrödinger equation in elliptic coordinates. Basically, it imposes the condition that the wave function should vanish at $v=0$, but the specific form is important in the deduction of the virial relation. It may be noted that, since V_0 is ultimately taken to the limit of positive infinity, its being multiplied by the factor of $1/(u^2-v^2)$ will not affect the barrier nature of the potential in (2.1), which mainly implies that the wave function vanishes at the boundary.

The Schrödinger equation for the hydrogen atom in half space, in elliptic coordinates, is

$$-\frac{1}{2}(\frac{2}{R})^2\frac{1}{(u^2-v^2)}\Big[\frac{\partial}{\partial u}(u^2-1)\frac{\partial}{\partial u} + \frac{\partial}{\partial v}(1-v^2)\frac{\partial}{\partial v}$$
$$+ \big(\frac{1}{u^2-1} + \frac{1}{1-v^2}\big)\frac{\partial^2}{\partial\phi^2}\Big]\psi + V\psi = E\psi. \tag{2.4}$$

The equation is separable, and by writing

$$\psi(u,v,\phi) = A(u^2-1)^{|m|/2}(1-v^2)^{|m|/2} \cdot F(u)G(v)e^{im\phi} \tag{2.5}$$

we obtain

$$(u^2-1)\frac{\mathrm{d}^2F}{\mathrm{d}u^2} + 2(|m|+1)u\frac{\mathrm{d}F}{\mathrm{d}u} + ZRuF + \frac{1}{2}R^2E(u^2-1)F = \beta F, \quad u \geq 1, \tag{2.6}$$

$$(1-v^2)\frac{\mathrm{d}^2G}{\mathrm{d}v^2} - 2(|m|+1)v\frac{\mathrm{d}G}{\mathrm{d}v} - ZRvG\frac{1}{2}R^2V_0\theta(v)G + \frac{1}{2}R^2E(1-v^2)G = -\beta G, \; |v| \leq 1, \tag{2.7}$$

where β is the separation constant. It may be noted that our separation constant β is different from the separation constant A' used by Shan et al. [6]. The reason for this is that they separate out the u and v components in (2.4) before taking out the $(u^2-1)^{|m|/2}$ and $(1-v^2)^{|m|/2}$ factors in (2.5). This leads to some additional terms from the derivatives of these factors. Our separation constant β is related to the separation constant A' of Shan et al. [6], as

$$\beta = -A' - |m|(|m|+1). \tag{2.8}$$

Since we will concentrate mainly on (2.6) and (2.7), we prefer to use β as the separation constant. The barrier term in (2.7) requires that $G(v)$ should vanish at $v=0$, for $V_0 \to \infty$. We now analyse some general properties of the solutions.

2.2. Asymptotic Behaviour

For determining the asymptotic behaviour of $F(u)$, we first note that

$$\frac{\mathrm{d}^2F}{\mathrm{d}u^2} \to -\frac{1}{2}R^2EF \quad \text{for} \quad u \to \infty, \tag{2.9}$$

which implies that

$$F(u) \to e^{-\alpha u}, \quad \alpha = \frac{1}{2}R(-2E)^{1/2}, \quad \text{for } u \to \infty. \tag{2.10}$$

To obtain the more general asymptotic behaviour, we consider

$$F = e^{-\alpha u}\sum_{i=0} C_i u^{b-i}. \tag{2.11}$$

Substituting this in (2.6) and equating the coefficients of successive power terms in u, we get from the first two equations

$$\alpha = \frac{1}{2}R(-2E)^{1/2}, \tag{2.12}$$

$$b = \frac{ZR}{2\alpha} - (|m|+1).$$

Though the power term is of some significance, the dominant part of the asymptotic behaviour is the exponential term with the exponent related to the energy as in (2.10) and (2.12).

2.3. Coalescence Condition

When the electron is close to the nucleus, it corresponds to $u \to 1$ and $v \to -1$. In this limit (2.6) and (2.7) lead to

$$2(|m|+1)\frac{1}{F}\frac{\mathrm{d}F}{\mathrm{d}u}\Big|_{u=1} + ZR = \beta,$$

$$-2(|m|+1)\frac{1}{G}\frac{\mathrm{d}G}{\mathrm{d}v}\Big|_{v=-1} - ZR = \beta. \tag{2.13}$$

Equating the two, one gets

$$\frac{1}{F}\frac{\mathrm{d}F}{\mathrm{d}u}\Big|_{u=1} + \frac{1}{G}\frac{\mathrm{d}G}{\mathrm{d}v}\Big|_{v=-1} = -\frac{ZR}{|m|+1}, \tag{2.14}$$

which may be described as the coalescence property [10] of the wave function when the electron approaches the nucleus.

2.4. Inflection Property

Since the potential barrier with $V_0 \to \infty$ at $v = 0$ implies that the wave function vanishes at $v = 0$, one obtains from (2.7)

$$\frac{\mathrm{d}^2 G}{\mathrm{d}v^2}\Big|_{v=0} = 0. \tag{2.15}$$

This may be described as the inflection property [11] of the wave function at the boundary. It is essentially a consequence of the fact, that when the wave function vanishes at a point, the remaining derivative terms in the Schrödinger equation together should also vanish at that point. For example, for the one particle case, $\nabla^2\psi$ should vanish at the points where ψ vanishes. When the solutions are available in the factorized form, it leads to the simpler inflection property related to the corresponding wave function, e.g. as in (2.15). This property is applicable to all wave functions which vanish at a point and which are in the factorized form, negative and positive energy wave functions. The inflection property is a simple property but useful in developing model wave functions.

2.5. Virial Relation

A virial relation for the energy eigenstates is a very useful relation especially for the excited states. The general virial relation for the energy eigenstates is

$$< \frac{p^2}{2} >= \frac{1}{2} < \boldsymbol{r}_1 \cdot \nabla_1 V > . \tag{2.16}$$

For the potential in (2.3) one obtains

$$\boldsymbol{r}_1 \cdot \nabla_1 V = \frac{Z}{r_1} + V_0 \frac{1}{u^2 - v^2}\frac{1}{R}\boldsymbol{r}_1 \cdot \Big(\frac{\boldsymbol{r}_1}{r_1} - \frac{\boldsymbol{r}_2}{r_2}\Big)\delta(v), \tag{2.17}$$

which then leads to

$$< \frac{p^2}{2} >= \frac{1}{2} < \frac{Z}{r_1} > + \frac{1}{2}V_0 < \frac{1}{u^3}\delta(v) > . \tag{2.18}$$

Using the wave function in (2.5), one gets for the second term

$$\frac{1}{2}V_0 < \frac{1}{u^3}\delta(v) >= \pi\Big(\frac{R}{2}\Big)^3 |A|^2 V_0 [G(0)]^2 \cdot \int_1^\infty \mathrm{d}u \frac{1}{u}(u^2-1)^{|m|}[F(u)]^2. \tag{2.19}$$

Finally, it may be noted that, when the electron is inside the barrier, (2.7) implies that

$$G \sim e^{-R(V_0/2)^{1/2}v} \quad \text{for } v > 0, \tag{2.20}$$

which then leads to

$$[G'(0)]^2 = \frac{1}{2}R^2 V_0 [G(0)]^2, \tag{2.21}$$

where $G'(v)$ represents the derivative of $G(v)$. Using the relation in (2.19), we finally get the virial relation

$$< \frac{p^2}{2} >= \frac{1}{2} < \frac{Z}{r_1} > + \frac{1}{4}\pi R|A|^2[G'(0)]^2 \cdot \int_1^\infty \mathrm{d}u \frac{1}{u}(u^2-1)^{|m|}[F(u)]^2!. \quad (2.22)$$

This relation will be used in developing model wave functions for the excited states.

2.6. Solutions for $R \to \infty$

For large values of R, the wave function is concentrated mainly around the nucleus at the upper focus $(0,0,-R/2)$, and the vanishing of the wave function at $v=0$ is not an important constraint. In this domain, we have essentially the Coulombic solutions, but in elliptic coordinates. In this case, ignoring the barrier term in (2.7), we note that the equations for $F(u)$ and $G(v)$ are identical except that they are relevant in different regions. Therefore, the wave functions can be written as products of $F(u)$ and $G(v)$, which are identical functions in the form

$$\psi(u,v,\phi) = A(u^2-1)^{|m|/2}(1-v^2)^{|m|/2}F(u)F(v)e^{im\phi} \quad \text{for } R \to \infty. \quad (2.23)$$

Therefore we need to obtain solutions only for $F(u)$.

For obtaining the solutions for $F(u)$, we separate out the asymptotic behaviour

$$F(u) = e^{-\alpha R u/2} f(u), \quad \alpha = (-2E)^{1/2}, \quad (2.24)$$

to obtain from (2.5)

$$(u^2-1)\frac{\mathrm{d}^2 f}{\mathrm{d}u^2} - [\alpha R(u^2-1) - 2(|m|+1)u]\frac{\mathrm{d}f}{\mathrm{d}u} + [ZRu - \alpha R(|m|+1)u - \beta]f = 0. \quad (2.25)$$

We substitute

$$f(u) = \sum_{i=0} C_i x^i, \quad x = u-1, \quad (2.26)$$

in (2.25) and equate the coefficients of x^i to get

$$C_{i+1} = \frac{1}{2(i+1)(i+|m|+1)} \cdot [-\{i(i+2|m|+1-2\alpha R) - \alpha R(|m|+1) + ZR - \beta\}C_i + \{\alpha R(i+|m|) - ZR\}C_{i-1}]. \quad (2.27)$$

Now, though this is a three term recursion relation since there are two free parameters, the energy E and separation constant β, one can terminate the series and obtain normalizable solutions for $F(u)$ and $G(v)$. Taking

$$C_i = 0 \quad \text{for} \quad \mathrm{i} \geq \mathrm{n}+1, \quad (2.28)$$

we have from (2.27) for $i = n, n+1$,

$$[n(n+2|m|+1-2\alpha R) - \alpha R(|m|+1) + ZR - \beta]C_n = [\alpha R(n+|m|) - ZR]C_{n-1}, \quad (2.29)$$

$$\alpha R(n+|m|+1) - ZR = 0. \quad (2.30)$$

With α in (2.24) we have for the bound state energies

$$E = -\frac{Z^2}{2(n+|m|+1)^2}, \quad n = 0,1,\ldots, \quad (2.31)$$

which of course agrees with the usual Coulombic energies. Then (2.29) determines the separation constant. With the use of (2.27) for obtaining successive C_i, (2.29) reduces to an algebraic equation of order $(n+1)$ in β. To be specific, we have

$$E = -\frac{Z^2}{2(|m|+1)^2}, \quad \beta = 0 \quad (2.32)$$

for $n=0$, and the corresponding wave function is

$$\psi(u,v,\phi) = A(u^2-1)^{|m|/2}(1-v^2)^{|m|/2}F(u)F(v)e^{im\phi},$$

$$F(u) = e^{-\frac{1}{2}ZRu/(|m|+1)}. \quad (2.33)$$

In spherical coordinates this reduces to

$$\psi(u,v,\phi) = B r_1^{|m|} e^{-Zr_1/(|m|+1)} (\sin\theta_1)^{|m|} e^{im\phi}. \quad (2.34)$$

For $n=1$, we get two solutions:

$$E = -\frac{Z^2}{2(|m|+2)^2}, \quad (2.35)$$

$$\beta = 1+|m| \pm \left[(1+|m|)^2 + \alpha^2 R^2\right]^{1/2},$$

$$\alpha = Z/(|m|+2),$$

with the corresponding wave functions

$$\psi(u,v,\phi) = A(u^2-1)^{|m|/2}(1-v^2)^{|m|/2}F(u)F(v)e^{im\phi},$$

$$F(u) = [C_0 + (u-1)C_1]e^{-\frac{1}{2}ZRu/(|m|+2)},$$

$$C_1 = \frac{1}{2(|m|+1)}[\alpha R(|m|+1) - ZR + \beta]C_0. \qquad (2.36)$$

The main feature of the solutions is that for $R \to \infty$, the solutions are given in terms of identical functions of u and v.

2.7. Solutions for $R \to 0$

In the limit of $R \to 0$ one has $u \to 2r/R$ and $v \to -\cos\theta$, where r and θ are the spherical coordinates. The equations (2.6) and (2.7) reduce [5] to the radial and angular equations in spherical coordinates. We therefore have the usual Coulombic solutions with the additional constraint that the wave functions should vanish at $\theta = \pi/2$. This imposes the condition that $l+m$ in the Coulombic solutions should be an odd integer. Indeed, since the wave functions in this limit are products of angular and radial parts with well-defined l and m quantum numbers, it is appropriate to designate the hydrogenic states in half space in terms of the states for $R \to 0$. In the usual notation [3], these states would be $2p\sigma$, $3p\sigma$, $3d\pi$, $4f\sigma$ etc.

2.8. Nucleus Inside the Barrier

For the nucleus inside the potential barrier, we can carry out a similar analysis with the $-1/r_1$ term in (2.3) replaced by the $-1/r_2$ term and the $-ZRvG(v)$ term in (2.7) replaced by the $ZRvG(v)$ term. This also is an interesting case of an impurity located inside the barrier plane.

3. Numerical Solutions

Numerical solutions have been obtained by several approaches, using infinite continued fractions [1], truncated matrix equations [6], the Killingbeck method [7], eigenfunction expansion [8] etc. It would, however, be useful to develop a simple method for obtaining the solutions. Here we describe an elementary approach for obtaining solutions to (2.6) and (2.7). These equations have two parameters, the energy E and separation constant β, which are determined by the requirement that the solutions are bounded and non-singular in the physical domains, $u : (1,\infty)$, and $v : (-1,0)$.

For obtaining the solutions for $F(u)$ and $G(v)$, it is convenient to use the variables

$$u_1 = u - 1, \quad v_2 = v + 1, \qquad (3.1)$$

in terms of which (2.6) and (2.7) lead to

$$u_1(u_1+2)\frac{\mathrm{d}^2F}{\mathrm{d}u_1^2} + 2(|m|+1)(u_1+1)\frac{\mathrm{d}F}{\mathrm{d}u_1} + ZR(u_1+1)F + \frac{1}{2}R^2Eu_1(u_1+2)F - \beta F = 0, \qquad (3.2)$$

$$v_2(v_2-2)\frac{\mathrm{d}^2G}{\mathrm{d}v_2^2} + 2(|m|+1)(v_2-1)\frac{\mathrm{d}G}{\mathrm{d}v_2} + ZR(v_2-1)G + \frac{1}{2}R^2Ev_2(v_2-2)G - \beta G = 0. \qquad (3.3)$$

With the series expansions

$$F = \sum_{i=0} C_i u_1^i, \quad G = \sum_{i=0} D_i v_2^i, \qquad (3.4)$$

we get the recursion relations

$$C_{i+1} = -\frac{[i(i+2|m|+1) + ZR - \beta]C_i + (ZR + R^2E)C_{i-1} + \frac{1}{2}R^2EC_{i-2}}{2(i+1)(i+|m|+1)}, \qquad (3.5)$$

$$D_{i+1} = \frac{[i(i+2|m|+1) - ZR - \beta]D_i + (ZR - R^2E)D_{i-1} + \frac{1}{2}R^2ED_{i-2}}{2(i+1)(i+|m|+1)}. \qquad (3.6)$$

Now requiring that $G(v) = 0$ at $v = 0$ or $v_2 = 1$ leads to the condition

$$\sum_{i=0} D_i = 0. \qquad (3.7)$$

Since

$$D_{i+1}/D_i \to \frac{1}{2} \quad \text{for} \quad i \to \infty, \tag{3.8}$$

it is adequate to sum over the first 100 terms with D_i obtained from the recursion relation in (3.6). Thus (3.7) is one constraint on the parameters E and β. For obtaining bounded solutions for $F(u)$, we first use the series in (3.5) to obtain the solutions at $u_1 = 1/2 - \Delta$ and $u_1 = 1/2$ for small Δ. Then we continue to higher values of u_1 by converting (3.2) into a difference equation, which leads to

$$F(u_1+\Delta) = \tag{3.9}$$

$$\frac{(2h_2 - h_0\Delta^2)F(u_1) + (-h_2 + h_1\Delta/2)F(u_1-\Delta)}{h_2 + h_1\Delta/2}$$

with

$$h_0 = ZR(u_1+1) + \frac{1}{2}R^2 E u_1(u_1+2) - \beta,$$

$$h_1 = 2(|m|+1)(u_1+1),$$

$$h_2 = u_1(u_1+2). \tag{3.10}$$

We then require that $F(u_1) \to 0$ for $u_1 \to \infty$, which imposes another condition on E and β. Thus the separation constant β and energy E are determined from the condition in (3.7) that $G(0) = 0$, and the condition that the continued solution for $F(u_1)$ in (3.9) vanishes at infinity for, which we can approximate it by taking u_1 to be about $100/R$.

We have presented our results for the energies E and the separation constants β in Tables 1 and 2, for the states $2p\sigma$, $3p\sigma$, $4f\sigma$ and $3d\pi$. The results of our very simple approach agree with the results of Shan et al. [6]. We have also presented our results for the nucleus inside the potential barrier, at $(0,0,-R/2)$. As mentioned before, this is equivalent to changing the $-1/r_1$ term in (2.3) to $-1/r_2$. The corresponding results are indicated in Tables 1 and 2 by placing the symbol $(-)$ after the values of R. The energies are plotted in Fig. 1 as functions of R, to provide a qualitative understanding of the variation. It may be noted that for large values of R, the excited states are pushed up slightly, whereas the ground state energy is not affected significantly. For smaller values of R, the ground state energy increases significantly, whereas the changes in the excited state energies are relatively smaller. What this implies is that, when the confining radius R decreases from large values, at first the energy differences between the excited states and the ground state increase slightly, but then start decreasing for smaller values of R. It would be very interesting to observe this in terms of the corresponding variations in the spectral properties.

Table 1. The numerically calculated values of the energies E and the corresponding separation constant β, for $2p\sigma$ and $3p\sigma$ states, for some values of R. The entries with $(-)$ in the bracket correspond to the nucleus inside the potential barrier at $(0,0,-R/2)$.

	— $2p\sigma$ —		— $3p\sigma$ —	
R	β	E	β	E
10.0	0.0025	–0.4998	–4.03	–0.1242
8.0	0.0118	–0.4987	–2.99	–0.1231
6.0	0.0516	–0.4927	–1.90	–0.1204
5.0	0.1033	–0.4830	–1.33	–0.1178
4.0	0.202	–0.4609	–0.731	–0.1137
3.0	0.384	–0.4111	–0.105	–0.1065
2.5	0.527	–0.3678	0.221	–0.1009
2.0	0.718	–0.3086	0.556	–0.09302
1.5	0.970	–0.2395	0.902	–0.08222
1.0	1.282	–0.1805	1.260	–0.07025
0.5	1.631	–0.1450	1.627	–0.06125
0.5(–)	2.380	–0.1119	2.377	–0.05157
1.0(–)	2.767	–0.1022	2.756	–0.04847
1.5(–)	3.161	–0.09461	3.138	–0.04594
2.0(–)	3.559	–0.08839	3.522	–0.04379
3.0(–)	4.368	–0.07868	4.294	–0.04031
5.0(–)	6.019	–0.06553	5.851	–0.03529

Table 2. The numerically calculated values of the energies E and the corresponding separation constant β, for $4f\sigma$ and $3d\pi$ states, for some values of R. The entries with $(-)$ in the bracket correspond to the nucleus inside the potential barrier at $(0,0,-R/2)$.

	— $4f\sigma$ —		— $3d\pi$ —	
R	β	E	β	E
10	7.67	–0.08277	0.376	–0.11859
8	7.82	–0.06141	0.658	–0.11240
6	8.53	–0.04680	1.116	–0.10135
5	9.01	–0.04251	1.435	–0.09357
4	9.55	–0.03930	1.826	–0.08464
3	10.12	–0.03674	2.289	–0.07552
2.5	10.42	–0.03563	2.545	–0.07127
2.0	10.73	–0.03462	2.815	–0.06737
1.5	11.04	–0.03368	3.097	–0.06387
1.0	11.35	–0.03281	3.390	–0.06076
0.5	11.67	–0.03201	3.691	–0.05801
0.5(–)	12.33	–0.03053	4.32	–0.05336
1.0(–)	12.66	–0.02986	4.64	–0.05138
1.5(–)	13.00	–0.02923	4.96	–0.04959
2.0(–)	13.35	–0.02863	5.30	–0.04795
3.0(–)	14.04	–0.02752	5.97	–0.04507
5.0(–)	15.47	–0.02560	7.36	–0.04044

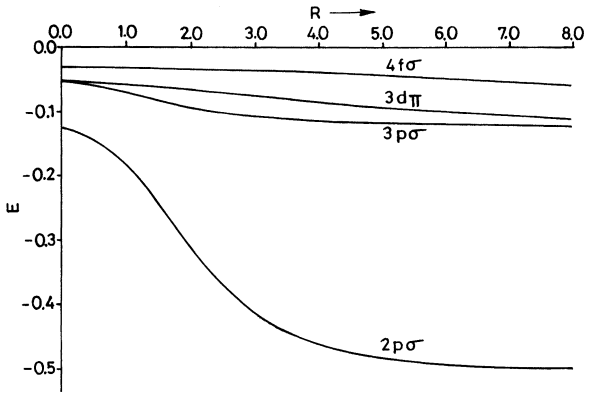

Fig. 1. Energies of the $2p\sigma$, $3p\sigma$, $4f\sigma$, and $3d\pi$ states, as functions of R where $R/2$ is the distance of the nucleus from the infinite barrier.

4. Model Wave Functions

We now develop some model wave functions incorporating the general properties we have discussed, which yield accurate values for the properties of the hydrogenic system in half space and which give an insight into their physical structure.

4.1. Ground State Wave Function

For the ground state, we consider a wave function

$$\begin{aligned} \psi_0 &= AF(u)G(v), \\ F(u) &= (1+au)e^{-\alpha u}, \\ G(v) &= \sinh(\alpha v), \\ \alpha &= \frac{1}{2}R(-2E)^{1/2}. \end{aligned} \tag{4.1}$$

This wave function incorporates the asymptotic behaviour in (2.10) and the inflection property in (2.15). We determine the parameter a by using the coalescence property in (2.14), which leads to

$$a = \frac{\alpha - R + \alpha\coth(\alpha)}{-\alpha + 1 + R - \alpha\coth(\alpha)}. \tag{4.2}$$

Thus, the parameters α and a are related to the energy E which is determined iteratively by requiring that the input energy and the output energy

$$E = \frac{<\psi_0|H|\psi_0>}{<\psi_0|\psi_0>} \tag{4.3}$$

are equal. Only about 2 or 3 iterations are required for obtaining an equality to 4 decimal places. It may also be noted that for large R, this form incorporates the property in (2.23). To see this, one notes that α is large for large R, and since v is in the range $(-1,0)$, the dominant part of our wave function in (4.1) for negative values of v is of the same form as the wave function in (2.23) for $m = 0$.

Table 3. The energies E predicted by the model wave function in (4.1) for the ground state, i. e. $2p\sigma$ state, normalization constant A, expectation values $<r_1>, <z_1>, <1/r_1>$, and the virial ratio V_r defined in (4.4), for some values of R.

R	A	$<r_1>$	$<z_1>$	$<1/r_1>$	E	V_r
10.0	1.131	1.496	0.0053	1.001	−0.49978	1.00
8.0	1.143	1.484	0.0204	1.006	−0.49868	1.00
6.0	1.187	1.449	0.0691	1.023	−0.49257	1.00
5.0	1.242	1.417	0.1203	1.043	−0.48260	1.01
4.0	1.338	1.378	0.2038	1.074	−0.45949	1.00
3.0	1.490	1.359	0.3497	1.104	−0.40666	1.00
2.5	1.565	1.402	0.4815	1.092	−0.36099	0.99
2.0	1.541	1.596	0.7410	0.9950	−0.30179	0.99
1.5	1.197	2.247	1.352	0.7249	−0.23713	1.02
1.0	0.5750	3.441	2.363	0.4228	−0.17942	1.06
0.5	0.1701	4.404	3.194	0.2958	−0.14440	1.05
0.2	0.0507	4.788	3.547	0.2642	−0.13172	1.02
0.1	0.0231	4.897	3.651	0.2566	−0.12823	1.01

The calculated values of the energy E, and some relevant expectation values obtained from our wave function are given in Table 3. The calculations involve simple integrations. Some of the details are given in the appendix A. The values of the energies are close to the numerically calculated values. It may also be noted that the virial ratio

$$V_r = \frac{<\boldsymbol{r}_1 \cdot \nabla_1 V>}{<p^2>}, \tag{4.4}$$

which is the ratio of the terms on the right-hand and left-hand side of (2.22), should be 1 for the exact energy eigenfunctions. The values of this ratio, calculated by using the expressions in (2.22) with our wave function, are close to 1. It must be emphasized that our wave function is essentially parameter-free, but incorporates the asymptotic property, coalescence property, inflection property, and the property for large R. The accuracy of the predictions emphasizes the importance of these structural properties.

There are some interesting implications of the results. It may be noted that, when R decreases from large values, $<r_1>$ decreases up to $R \approx 3.0$. This may be regarded as a consequence of the compression of the electron cloud between the nucleus and the potential barrier. However, for R less than 3.0, $<r_1>$ increases to about 5.0 for $R \to 0$. This is the consequence of the property that the binding energy of the

electron decreases for smaller values of R and the electron becomes more loosely bound. Another interesting property is that when R decreases, $< z_1 >$ increases, which implies that the potential barrier induces an electric dipole in the atom which increases as R decreases. It also implies that, when there are two hydrogen atoms near an impenetrable surface, the dominant interaction between them at large separations will be due to the interaction between the dipoles induced by the barrier,

$$V(1,2) = \frac{\boldsymbol{p}_1 \cdot \boldsymbol{p}_2}{r_{12}^3} - \frac{3\boldsymbol{p}_1 \cdot \boldsymbol{r}_{12}\, \boldsymbol{p}_2 \cdot \boldsymbol{r}_{12}}{r_{12}^5}, \tag{4.5}$$

where $\boldsymbol{p}_1 = -\boldsymbol{k} < z_1 >$, $\boldsymbol{p}_2 = -\boldsymbol{k} < z_2 >$ and $\boldsymbol{r}_{12}$ is the separation between the atoms. It would be very interesting to observe this potential for two hydrogen atoms near an impenetrable surface.

4.2. Lowest Energy State with $m = 1$

For the lowest energy state with $m = 1$ we take a wave function

$$\begin{aligned} \psi_1 &= A(u^2-1)^{1/2}(1-v^2)^{1/2}F(u)G(v)e^{i\phi}, \\ F(u) &= (1+au)e^{-\alpha u}, \\ G(v) &= \sinh(\alpha v), \\ \alpha &= \frac{1}{2}R(-2E)^{1/2}. \end{aligned} \tag{4.6}$$

This wave function also incorporates the asymptotic behaviour in (2.10) the inflection property in (2.15), and the property in (2.23) for large R. The parameter a is again determined by using the coalescence property in (2.14) which leads to

$$a = \frac{\alpha - R/2 + \alpha\coth(\alpha)}{-\alpha + 1 + R/2 - \alpha\coth(\alpha)}. \tag{4.7}$$

The energy is determined iteratively, so that the input energy E and the output energy

$$E = \frac{< \psi_1 | H | \psi_1 >}{< \psi_1 | \psi_1 >} \tag{4.8}$$

are equal. Some of the details of the calculations are given in appendix A.

The calculated values of the energy E, and some relevant expectation values obtained from our wave function in (4.6) are given in Table 4. The predicted values of the energies are close to the numerically calculated values, and the virial ratio in (4.4), which is the ratio of the right-hand and left-hand side of (2.22), is close to 1. This indicates the good quality of the wave functions based on the general structural properties.

Table 4. The energies E predicted by the model wave function in (4.6) for the lowest energy state with $m = 1$, i.e. the $3d\pi$ state, normalization constant A, expectation values $< r_1 >$, $< z_1 >$, $< 1/r_1 >$, and the virial ratio V_r defined in (4.4), for some values of R.

R	A	$<r_1>$	$<z_1>$	$<1/r_1>$	E	V_r
15.0	1.106	4.899	0.1260	0.2537	−0.12392	1.00
10.0	0.8519	4.674	0.4333	0.2653	−0.11818	1.00
8.0	0.7644	4.536	0.6715	0.2741	−0.11118	0.99
6.0	0.6406	4.511	1.089	0.2784	−0.09839	0.97
5.0	0.5136	4.814	1.542	0.2647	−0.09068	0.96
4.0	0.3282	5.702	2.384	0.2272	−0.08328	0.99
3.0	0.1508	7.146	3.579	0.1781	−0.07520	1.02
2.5	$8.79\cdot10^{-2}$	7.907	4.200	0.1576	−0.07104	1.04
2.0	$4.58\cdot10^{-2}$	8.594	4.775	0.1420	−0.06714	1.05
1.5	$2.07\cdot10^{-2}$	9.181	5.289	0.1307	−0.06368	1.04
1.0	$7.42\cdot10^{-3}$	9.678	5.748	0.1224	−0.06065	1.03
0.5	$1.50\cdot10^{-3}$	10.11	6.167	0.1162	−0.05798	1.02
0.2	$2.13\cdot10^{-4}$	10.35	6.407	0.1130	−0.05650	1.01
0.1	$5.12\cdot10^{-5}$	10.42	6.485	0.1121	−0.05602	1.00

4.3. First Excited State with $m = 0$

For the excited states, there is a tendency for the model wave functions to collapse to the ground states. This we avoid by requiring that the wave function satisfies the virial relation in (2.22), which is a property satisfied by the eigenstates of energy. For the first excited state with $m = 0$ we choose a model wave function

$$\begin{aligned} \psi_2 &= AF(u)G(v), \\ F(u) &= (1+au+bu^2)e^{-\alpha u}, \\ G(v) &= \sinh(\alpha v) - av\cosh(\alpha v), \\ \alpha &= \frac{1}{2}R(-2E)^{1/2}. \end{aligned} \tag{4.9}$$

This form conforms with the property in (2.23) that $F(u)$ and $G(v)$ tend to the same form for $R \to \infty$. To see this, it may be noted that α is large for large R, and since v is in the range $(-1,0)$, the dominant part of $G(v)$ in (4.9) tends to $F(u)$ with $b \to 0$. Our wave function in (4.9) incorporates the asymptotic behaviour in (2.10) and the inflection property in (2.15). We determine the parameter b by using the coalescence property in (2.14), which leads to

$$b = -1 - a + \frac{(a+2)(a-\tanh(\alpha))}{(2-\alpha+R)(a-\tanh(\alpha)) + \alpha - a - a\alpha\tanh(\alpha)}. \tag{4.10}$$

Table 5. The energies E predicted by the model wave function in (4.9) for the first excited state with $m = 0$, i. e. the $3p\sigma$ state, the values of the parameters a obtained by using the virial relation in (2.22), normalization constant A, and expectation values $< r_1 >$, $< z_1 >$, $< 1/r_1 >$, for some values of R.

R	a	A	$< r_1 >$	$< z_1 >$	$< 1/r_1 >$	E
15.0	−0.878	1.290	5.56	2.99	0.2505	−0.12491
10.0	−0.829	0.957	5.55	3.04	0.2523	−0.12419
8.0	−0.795	0.831	5.55	3.11	0.2539	−0.12304
6.0	−0.737	0.711	5.58	3.27	0.2553	−0.12030
5.0	−0.691	0.657	5.63	3.39	0.2554	−0.11766
4.0	−0.621	0.607	5.75	3.61	0.2534	−0.11343
3.0	−0.508	0.570	6.09	4.00	0.2458	−0.10618
2.5	−0.420	0.578	6.42	4.33	0.2417	−0.10048
2.0	−0.294	0.619	7.08	4.91	0.2342	−0.09228
1.5	−0.089	0.775	8.38	5.97	0.2204	−0.08195
1.0	0.1534	4.456	9.96	7.20	0.1777	−0.0703
0.5	1.74	$8.12 \cdot 10^{-3}$	11.53	8.54	0.1299	−0.0615

The remaining parameter a is determined by requiring that the virial relation in (2.22) is satisfied. The calculations are similar to those for the ground state, except for the extra terms in $F(u)$ and $G(v)$. The energy E is determined iteratively, so that the input energy E in (4.9) and the output energy

$$E = \frac{< \psi_2 | H | \psi_2 >}{< \psi_2 | \psi_2 >} \tag{4.11}$$

are equal. The calculated values of the energy E and some relevant expectation values obtained from our model wave function are given in Table 5. The values of the energy are close to the numerically calculated values. This again emphasizes the importance of the structural properties of the wave functions and the virial relation in (2.22) in the development of model wave functions.

4.4. Perturbative Solutions

When the nucleus is on the barrier surface, we have the exact hydrogenic solutions with odd values for $l + m$. Therefore, when the nucleus is slightly above the surface, we can analyse the problem perturbatively with

$$\begin{aligned} V &= -\frac{1}{r} \quad \text{for} \quad z > 0 \\ &= \infty \quad \text{for} \quad z \le 0 \end{aligned} \tag{4.12}$$

being the unperturbed potential, and

$$V_p = \frac{1}{r} - \frac{1}{|\boldsymbol{r} - \boldsymbol{R}/2|} \tag{4.13}$$

being the perturbation potential. Then the energy, correct to first order in the perturbation, is given by

$$E = -\frac{1}{2(n_r + l + 1)^2} + < \psi | V_p | \psi >, \tag{4.14}$$

where n_r is the radial quantum number and $l + m$ is an odd integer. For example, for the ground state, i.e. $2p\sigma$ state, we have

$$\begin{aligned} \psi_0(r, \theta, \phi) &= A r \cos(\theta) e^{-r/2} \quad \text{for} \quad \theta < \pi/2 \\ &= 0 \quad \text{for} \quad \theta \ge \pi/2 \end{aligned} \tag{4.15}$$

for the unperturbed wave function, so that for small R we get

$$E = -\frac{1}{8} - \frac{R}{32}, \quad \text{for small } R. \tag{4.16}$$

This gives reasonable values for $R \le 0.5$. For example, for $R = 0.5$ it gives $E = -0.1406$, whereas the accurate, numerical value is $E = -0.1450$.

5. Helium Atom in Half Space

Here we extend our analysis to deduce the energies of He atom in half space.

5.1. Scaling Property

The properties of the hydrogen atom with nuclear charge 1 can be extended to a one-electron system with nuclear charge Z by a scale transformation. With the scale transformation, the Schrödinger equation in half space for the system with nuclear charge Z takes the form

$$\begin{aligned} -\frac{1}{2} \nabla'^2 \psi(\lambda \boldsymbol{r}', Z, R) - \frac{Z\lambda}{|\boldsymbol{r}' - \boldsymbol{R}/2|} \psi(\lambda \boldsymbol{r}', Z, R) \\ = \lambda^2 E(Z, R) \psi(\lambda \boldsymbol{r}', Z, R), \\ \boldsymbol{r} = \lambda \boldsymbol{r}', \end{aligned} \tag{5.1}$$

with the boundary condition $\psi(z = 0) = 0$. Choosing $\lambda = 1/Z$, and comparing the equation with the hydrogenic equation, we get

$$\begin{aligned} E(Z, R) &= Z^2 E(1, ZR), \\ \psi(\boldsymbol{r}, Z, R) &= Z^{3/2} \psi(Z\boldsymbol{r}, 1, ZR). \end{aligned} \tag{5.2}$$

This allows us to obtain the energies for one electron ion with nuclear charge Z in terms of the hydrogenic energies.

5.2. Energies for He

For a He atom in half space, the hamiltonian is

$$H = \frac{1}{2}(p_1^2 + p_2^2) - Z(\frac{1}{r_1} + \frac{1}{r_2}) + \frac{1}{r_{12}} + V_0[\theta(-z_1) + \theta(-z_2)] \quad (5.3)$$

with $Z = 2$. We approximate the hamiltonian by taking

$$\frac{1}{r_{12}} = \delta(\frac{1}{r_1} + \frac{1}{r_2}). \quad (5.4)$$

This is a reasonable simulation for the ground state in terms of a screening effect. Then the hamiltonian decouples and the ground state energy is given by

$$E_2(Z,R) = -2(Z-\delta)^2\, E(1,(Z-\delta)R). \quad (5.5)$$

This gives the energy of the helium atom at a distance of $R/2$ from the plane, in terms of the hydrogenic energy with the nucleus at a distance $(Z-\delta)R/2$ from the plane. For obtaining a suitable expression for δ, we require that (5.5) gives the correct helium energy -2.9037 for $R \to \infty$, which implies that

$$\delta \to 0.2960 \quad \text{for } R \to \infty. \quad (5.6)$$

For $R = 0$ we can estimate $< 1/r_1 >$ and $< 1/r_{12} >$ by taking the unperturbed wave function of the form

$$\begin{aligned} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2) &= A z_1 z_2 e^{-Z(r_1+r_2)/2} \quad \text{for } z_1 > 0,\ z_2 > 0, \\ &= 0 \qquad \text{for } z_1 < 0 \text{ or } z_2 < 0. \end{aligned} \quad (5.7)$$

With this we get

$$< 1/r_1 > = Z/4 \quad (5.8)$$

and

$$\begin{aligned} < 1/r_{12} > &\approx 0.265Z, \\ &\approx 0.53(< 1/r_1 > + < 1/r_2 >). \end{aligned} \quad (5.9)$$

Including the correlation, we expect $< 1/r_{12} >$ to be smaller, and we take

$$\frac{1}{r_{12}} \approx 0.50(< \frac{1}{r_1} > + < \frac{1}{r_2} >) \quad \text{for } R = 0. \quad (5.10)$$

Combining the relations in (5.6) and (5.10), we take an interpolation

$$\delta = 0.296 + 0.204 e^{-ZR/2}, \quad (5.11)$$

which has the correct values for $R \to \infty$ and $R \to 0$. With this relation, we now have a simple expression in (5.5) for the ground state energy of He in half space. The energies $E_2(R)$ for some values of R, are

$$\begin{aligned} &E_2(5) = -2.894, \quad E_2(4) = -2.860, \\ &E_2(3) = -2.775, \quad E_2(2) = -2.407, \\ &E_2(1) = -1.366, \quad E_2(0.5) = -0.867. \end{aligned} \quad (5.12)$$

6. Discussion

We have considered some structural properties of the energy eigenfunctions of a hydrogenic system in half space. For the separable solutions in terms of elliptic coordinates we have analysed the asymptotic behaviour when the electron is far away from the nucleus, the coalescence property when the electron is close to the nucleus, the inflection property when the electron is close to the potential barrier, the factorization property when the nucleus is far away from the potential barrier, and the virial relation. These properties provide a clear insight into the structure of the wave functions, for example, the asymptotic behaviour gives a relation between the exponent of the asymptotic term and the energy of the system, and the vanishing of the wave function at the barrier surface implies the inflection property at the surface. We have then developed essentially parameter-free model wave functions for some states, incorporating these properties, which give accurate values for the energies and some other relevant quantities. This illustrates the importance of the structural properties in the development of simple and useful wave functions, which needs to be emphasized. These wave functions provide a physical understanding of the spectral and spatial properties of a hydrogenic system near a barrier, such as an electron and a heavy hole near a semi-conductor surface, impurity states or a hydrogen atom near a crystal surface. In particular, it may be noted that the induced dipole moment leads to a leading, long-range dipole-dipole interaction between two atoms. Finally we have considered the scaling properties of the energies and wave functions to obtain reliable estimates for the ground state energies of the helium atom in half space.

The author acknowledges C. S. I. R. support as an emeritus scientist.

Appendix A

We define integrals

$$u_n = \int_1^\infty u^n e^{-2\alpha u} \mathrm{d}u, \tag{A.1}$$

$$v_n = \int_{-1}^0 v^n [\sinh(\alpha v)]^2 \mathrm{d}v, \tag{A.2}$$

$$w_n = \int_{-1}^0 v^n \sinh(\alpha v)\cosh(\alpha v)\mathrm{d}v. \tag{A.3}$$

In terms of these integrals, the relevant expressions for some of the quantities for the ground state wave function ψ_0 in (4.1) are

$$\begin{aligned} <\psi_0|\psi_0> &= 2\pi(R/2)^3 \int_1^\infty \mathrm{d}u \int_{-1}^0 \mathrm{d}v (u^2-v^2)|AF(u)G(v)|^2 \\ &= 2\pi(R/2)^3|A|^2[(u_2+2au_3+a^2u_4)v_0-(u_0+2au_1+a^2u_2)v_2], \end{aligned} \tag{A.4}$$

$$\begin{aligned} <\psi_0|\frac{1}{2}p^2|\psi_0> &= -\frac{1}{2}2\pi(R/2)|A|^2 \int_1^\infty \mathrm{d}u \int_{-1}^0 \mathrm{d}v F(u)G(v)\big[\{(u^2-1)F''(u) \\ &\quad +2uF'(u)\}G(v)+F(u)\{(1-v^2)G''(v)-2vG'(v)\}\big] \\ &= -\frac{1}{2}2\pi(R/2)|A|^2\big[\{\alpha^2(u_2+2au_3+a^2u_4-u_0-2au_1-a^2u_2) \\ &\quad -2a\alpha(u_2+au_3-u_0-au_1)-2\alpha(u_1+2au_2+a^2u_3)+2a \\ &\quad (u_1+au_2)\}v_0+(u_0+2au_1+a^2u_2)\{\alpha^2(v_0-v_2)-2\alpha w_1\}\big], \end{aligned} \tag{A.5}$$

$$<\psi_0|\frac{1}{r_1}\psi_0> = 2\pi(R/2)^2|A|^2[(u_1+2au_2+a^2u_3)v_0-(u_0+2au_1+a^2u_2)v_1], \tag{A.6}$$

$$\begin{aligned} <\psi_0|r_1|\psi_0> &= 2\pi(R/2)^4|A|^2[(u_3+2au_4+a^2u_5)v_0-(u_1+2au_2+a^2u_3)v_2 \\ &\quad +(u_2+2au_3+a^2u_4)v_1-(u_0+2au_1+a^2u_2)v_3], \end{aligned} \tag{A.7}$$

$$\begin{aligned} <\psi_0|z_1|\psi_0> &= -\frac{R}{2}<(1+uv)> \\ &= -\frac{R}{2}-2\pi(R/2)^4|A|^2[(u_3+2au_4+a^2u_5)v_1 \\ &\quad -(u_1+2au_2+a^2u_3)v_3], \end{aligned} \tag{A.8}$$

and

$$\begin{aligned} \int_1^\infty \frac{1}{u}|F(u)|^2\mathrm{d}u &= \int_1^\infty \frac{1}{u}(1+au)^2e^{-2\alpha u}\mathrm{d}u \\ &= u_{-1}+2au_0+a^2u_1, \end{aligned} \tag{A.9}$$

$$G'(0) = \alpha, \tag{A.10}$$

which are required for evaluating the virial relation in (4.4).

For the lowest energy, $m = 1$ wave function in (4.6), one obtains

$$\begin{aligned} <\psi_1|\psi_1> &= 2\pi(R/2)^3[(u_2+2au_3+a^2u_4)(-v_0+v_4)+(u_0+2au_1+a^2u_2) \\ &\quad (v_2-v_4)+(u_4+2au_5+a^2u_6)(v_0-v_2)], \end{aligned} \tag{A.11}$$

$$\begin{aligned} <\psi_1|\frac{1}{2}p^2|\psi_1> &= -\frac{1}{2}2\pi(R/2)|A|^2\big[\{a^2\alpha^2(u_6-u_4)+(2a\alpha^2-6a^2\alpha) \\ &\quad (u_5-u_3)+(\alpha^2-10a\alpha+4a^2-a^2\alpha^2)(u_4-u_2)+ \\ &\quad (4a-4\alpha-2a\alpha^2+2a^2\alpha)(u_3-u_1)+(-\alpha^2+2a\alpha)(u_2-u_0)\} \\ &\quad (v_0-v_2)+\{(u_2+2au_3+a^2u_4)-(u_0+2au_1+a^2u_2)\} \\ &\quad \{\alpha^2(v_0-2v_2+v_4)-4\alpha(w_1-w_3)\}\big], \end{aligned} \tag{A.12}$$

and

$$\begin{aligned} <\psi_1|\frac{1}{r_1}|\psi_1> &= 2\pi(R/2)^2|A|^2[(u_0+2au_1+a^2u_2)(v_1-v_3)+(u_1+2au_2+a^2u_3) \\ &\quad (-v_0+v_2)+(u_2+2au_3+a^2u_4)(-v_1+v_3) \\ &\quad +(u_3+2au_4+a^2u_5)(v_0-v_2)]. \end{aligned} \tag{A.13}$$

[1] S. Satpathy, Phys. Rev. **B28**, 4585 (1983).
[2] Y. Shan, T. F. Jiang, and Y. C. Lee, Phys. Rev. **B31**, 5487 (1985).
[3] H. C. Tseng and Y. Shan, J. Phys. Condens. Matter **1**, 2225 (1989).
[4] A. Elmahboubi and Y. Lepine, J. Phys. Condens. Matter **7**, 7141 (1995).
[5] Y. Shan, J. Phys. **B20**, 4275 (1987).
[6] Y. Shan, P.-C. Lu, and H. C. Tseng, J. Phys. **B20**, 4285 (1987).
[7] G. Hadinger, M. Aubert-Frecon, A. Yanacopoulo, and G. Hadinger, J. Phys. **B24**, 1175 (1991).
[8] A. F. Kovalenko and M. F. Holovko, J. Phys. **B25**, L233 (1992).
[9] W. Jaskolski, Phys. Rep. **271**, 1 (1996).
[10] S. H. Patil, Phys. Rev. **A62**, 052515 (2000).
[11] S. H. Patil, J. Phys. **B35**, 255 (2002).