phys. stat. sol. 40, K59 (1970)

Subject classification: 13.4; 22

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Further Note on a Valence Electron Model of Atoms

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Wang (1) has introduced a "valence electron model of atoms" with the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_o}\left(\frac{I}{r} + \frac{C}{r^2}\right), \tag{1}$$

where I and C are constant parameters. Kunz (2) and Nickle (3) have discussed the possible values of C. Their treatment is, however, based on formal and even partly incorrect arguments deserving some complementary comments.

The radial Schrödinger equation corresponding to (1)

$$\frac{d^2R}{d\varrho^2} + \frac{2}{\varrho}\frac{dR}{d\varrho} + \left[-k^2 + \frac{2I}{\varrho} - \frac{\lambda(\lambda+1)}{\varrho^2}\right]R = 0 \tag{2}$$

is analogous to that of hydrogen-like atoms, with $\varrho = r/a_o$, $k^2 = -E/E_o$, and

$$\lambda(\lambda+1) = l(l+1) - \frac{2C}{a_o}, \tag{3}$$

where a_o is the Bohr radius and E_o the corresponding energy. It has the general solution $R = A\,f_1(\varrho) + B\,f_2(\varrho)$, where

$$\begin{aligned} f_1(\varrho) &= e^{-k\varrho}\,\varrho^{\lambda}\,F\left(1+\lambda-\frac{I}{k}\middle|\,2+2\lambda\middle|\,2k\varrho\right) \\ f_2(\varrho) &= e^{-k\varrho}\,\varrho^{-\lambda-1}F\left(-\lambda-\frac{I}{k}\middle|\,-2\lambda\middle|\,2k\varrho\right) \end{aligned} \tag{4}$$

in terms of the confluent hypergeometric function $F(a|c|z)$. Here we can write from (3)

$$\lambda = \begin{cases} -\frac{1}{2} + \sqrt{l(l+1) + \frac{1}{4} - \frac{2C}{a_o}} & \text{for } \frac{C}{a_o} \leq \frac{1}{8} + \frac{1}{2}l(l+1), \\ -\frac{1}{2} + i\sqrt{\frac{2C}{a_o} - l(l+1) - \frac{1}{4}} & \text{for } \frac{C}{a_o} \geq \frac{1}{8} + \frac{1}{2}l(l+1). \end{cases} \tag{5}$$

Choosing the minus sign for the square root would just change f_1 into f_2.

Discussing bound states we must look for normalizable solutions. At the origin this requires $f^* f \varrho^2 \sim \varrho^{-1+\epsilon}$ with $\epsilon > 0$. This leads us to a classification of the problem into three cases:

(i) $$\lambda > \frac{1}{2} \text{ or } \frac{C}{a_o} < -\frac{3}{8} + \frac{1}{2}l(l+1),$$

(ii) $$\frac{1}{2} \geq \lambda \geq -\frac{1}{2} \text{ or } -\frac{3}{8} + \frac{1}{2}l(l+1) \leq \frac{C}{a_o} \leq \frac{1}{8} + \frac{1}{2}l(l+1),$$

(iii) $$\lambda \text{ is complex or } \frac{C}{a_o} > \frac{1}{8} + \frac{1}{2}l(l+1).$$

In case (i) f_2 is ruled out by the behaviour at the origin, and f_1 is normalizable only if it terminates. This gives us the quantization rule

$$\epsilon = -\frac{E}{E_o} = \frac{I^2}{(n + \lambda + 1)^2}, \qquad n = 0, 1, 2, \ldots \tag{6}$$

of the energy. In the other two cases both f_1 and f_2 have acceptable behaviour at the origin, and the particular solution

$$R(\varrho) = D\left[\frac{\Gamma(-1-2\lambda)}{\Gamma(-\lambda - \frac{I}{k})} f_1 + \frac{\Gamma(1+2\lambda)}{\Gamma(1+\lambda - \frac{I}{k})\,(2k)^{1+2\lambda}} f_2\right] \tag{7}$$

is normalizable for all $E < 0$ (4). So we see that Nickle's extension of the energy quantization equation (6) to all real values of λ needs further justification.

Kunz discusses the possible non-Hermiticity, which is a basic but difficult problem (5). His proof, however, is incorrect, because it is based on unnormalizable

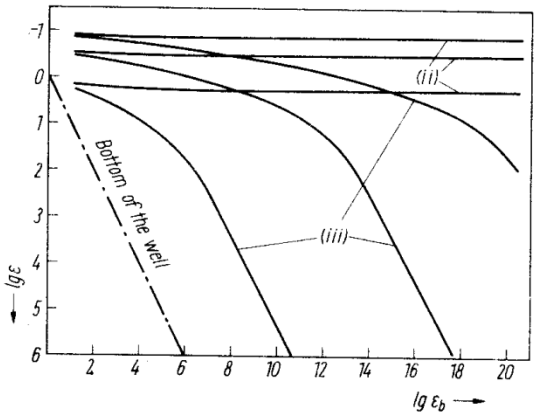

Fig. 1. The three lowest s levels in the truncated potential plotted against the well depth. The curves correspond to $C/a_o = 0.1$ (ii) and 0.2 (iii) close to the limiting value 0.125

test functions. Particularly, the continuous set of functions (7) is evidently not orthogonal. Therefore, in cases (ii) and (iii) either the model Hamiltonian is not Hermitian or the eigenfunctions of the problem are given by some discrete orthogonal subset of equation (7).

An instructive way to study this question is to treat the singular model Hamiltonian (1) as a limiting case of the regular one obtained by cutting out the singularity. If in the limit of zero cut-off radius the spectrum approaches a definite limit, the singularity is not essential for the problem. The spectrum of the singular Hamiltonian is then the limiting spectrum, and the eigenfunctions are the normalizable solutions (7) corresponding to the E values of this spectrum. The procedure assures the orthogonality and the completeness of the eigenfunctions and, hence, the Hermiticity of the Hamiltonian in the limit. In case (i) the normalizability is sufficient to fix the spectrum, while the other cases require closer examination.

The eigenvalues and eigenfunctions corresponding to the truncated non-singular potential

$$V(r; r_o) = \begin{cases} -\dfrac{e^2}{4\pi\epsilon_o}\left(\dfrac{I}{r} + \dfrac{C}{r^2}\right) & \text{for} \quad r \geq r_o \ , \\ -\dfrac{e^2}{4\pi\epsilon_o}\left(\dfrac{I}{r_o} + \dfrac{C}{r_o^2}\right) & \text{for} \quad r \leq r_o \ , \end{cases} \tag{8}$$

are obtained by the continuity requirement of the radial wavefunction and its derivative at r_o. The solution for $r \geq r_o$ is given by equation (7) and for $r \leq r_o$ it has the form of a spherical Bessel function. In order to demonstrate the nature of the problem we have studied numerically the dependence of the spectrum on the cut-off.

Fig. 1 shows the behaviour of the three lowest s levels ϵ_o, ϵ_1, and ϵ_2 in the potential well (8) as a function of its depth ϵ_b in cases (ii) and (iii) on both sides of the limiting value $C/a_o = 0.125$. Very close to the boundary the numerical difficulties increase greatly. The results indicate the existence of a well-defined limit in case (ii) showing that the differential operator (1) can be understood as a representation of an Hermitian operator. The spectrum is numerically equal to that given by equation (6), which justifies the formal extension of the termination rule. In case (iii) there is obviously no definite limit but each level will sink infinitely following the bottom of the well. The rule of the asymptotic behaviour is numerically equal to the rule

$$\frac{E_{n+1}}{E_n} = \exp\left(\frac{2\pi i}{\lambda + \frac{1}{2}}\right) = \exp\left(\frac{2\pi}{\sqrt{\frac{2C}{a_o} - l(l+1) - \frac{1}{4}}}\right)$$

derived for the case of r^{-2} potential (6) from the requirement of orthogonality. Thus, in case (iii) the procedure does not define any Hermitian operator, and the potential is too singular to be used as a model of any quantum mechanical problem.

In any case the singular Hamiltonian (1) is an unrealistic one at small values of r. The point is that in cases (i) and (ii) the states are not sensitive to the behaviour of the potential at small r, while in case (iii) they are. Therefore, if C is large, a more realistic short-range force must be included in the model when the states of low angular moments are treated.

The authors wish to thank P.O. Lipas for helpful discussions. Financial support from the National Research Council for Sciences, Finland and the North-Ostrobothnian Student Nation Scholarship Fund is gratefully acknowledged

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(Received June 6, 1970)