Boundary Conditions for the Relativistic Kronig-Penney Model*

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Relativistic corrections to the electronic states of heavy atomic crystals are investigated by solving the Dirac equation for the Kronig-Penney potential, subject to certain boundary conditions, which differ from those used in earlier studies. These new boundary conditions enable the mathematics to be simplified considerably, without obscuring any of the relativistic effects found previously. Comparisons are made between the results obtained using the different sets of boundary conditions.

I. INTRODUCTION

A RELATIVISTIC theory of heavy atomic solids[1] and their surfaces[2,3] has been formulated recently on the basis of the Kronig-Penney (KP) [4] model. The behavior of relativistic electrons in these systems was studied by solving the Dirac equation, subject to certain boundary conditions, which involved *both* components of the two-component spinor wave functions. Such boundary conditions required a further restriction, so that the correct nonrelativistic (NR) limit was obtained for the KP relation. Moreover, in dealing with the surface states, the analysis was found to be rather complicated.

From the relativistic point of view, even the highest electronic velocity in solid state physics is still sufficiently low to justify the assumption that the small component of the spinor is of much less importance than the large one. Thus, in the present paper, instead of matching both components of the spinor, only the large component and its derivative are matched across the potential discontinuity. The advantages of adopting these new boundary conditions are: (1) removal of the additional restriction in obtaining NR limit of the KP relation and (2) simplification of the mathematics in analysing the surface-state energy and existence condition, without loosing the previous useful classification of surface states. Such a procedure is not only a useful one, but also a very good approximation, as shown in the Appendix. Finally, unlike the Glasser and Davison (GD)[1] S-matrix approach, a more straightforward technique is used here to obtain the KP relation.

II. CONTINUITY CONDITIONS FOR DIRAC EQUATION

The two-component time-independent Dirac equation for the linear potential $V(x)$ is[1–3,5]

$$ihc\sigma_x\phi'-m_0c^2\sigma_z\phi=(E-V)\phi\,, \tag{1}$$

where $\sigma_{x,z}$ are the x- and z-component Pauli spin matrices, viz.,

$$\sigma_x=\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad \sigma_z=\begin{pmatrix}1&0\\0&-1\end{pmatrix}. \tag{2}$$

Using the two-component spinor

$$\phi=\begin{pmatrix}\phi_1\\\phi_2\end{pmatrix}, \tag{3}$$

Eq. (1) becomes

$$ihc\phi_1'=(\epsilon-V)\phi_2\,,\quad \epsilon=E-m_0c^2 \tag{4}$$

$$ihc\phi_2'=[(\epsilon-V)+2m_0c^2]\phi_1. \tag{5}$$

Decoupling (4) and (5) for a constant potential V gives

$$\phi_{1,2}''=-\rho_v^2\phi_{1,2}\,, \tag{6}$$

where

$$\rho_v^2=(\epsilon-V)[(\epsilon-V)+2m_0c^2]/h^2c^2. \tag{7}$$

In matrix form, the plane-wave solution of (6) is

$$\phi=\begin{pmatrix}\alpha_1\\\alpha_2\end{pmatrix}e^{i\rho_v x}+\begin{pmatrix}\beta_1\\\beta_2\end{pmatrix}e^{-i\rho_v x}, \tag{8}$$

in which, because of the coupling between the component equations (4) and (5),

$$\alpha_1=-\gamma\alpha_2\,,\quad \beta_1=\gamma\beta_2\,, \tag{9}$$

where

$$\gamma=(\epsilon-V)/hc\rho_v. \tag{10}$$

For a step-potential discontinuity at $x=0$, between the regions II and III, GD chose the continuity condition

$$\phi_{II}(0)=\phi_{III}(0)\,, \tag{11}$$

which amounts to matching the two components of the spinor across the discontinuity. From (4) and (5), it follows that the *matching* of the first and second components in (11), respectively, leads to a relation

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[1] M. L. Glasser and S. G. Davison, Intern. J. Quantum Chem. (to be published).

[2] S. G. Davison and M. Steślicka, J. Phys. C 2, 1802 (1969).

[3] S. G. Davison and J. D. Levine, in Solid State Physics, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, to be published).

[4] R. de L. Kronig and W. G. Penney, Proc. Roy. Soc. A130, 499 (1931).

[5] A. S. Davydov, *Quantum Mechanics* (Pergamon Press, Inc., Oxford, 1965), p. 222.

between the derivatives of the second and first components in the two regions, i.e., $\phi_{II}'(0) \neq \phi_{III}'(0)$. Thus, the matching of the spinor components results in a nonmatching of their slopes.

In solid state physics, where $v/c \ll 1$, ϕ_2 (large component) $\gg \phi_1$ (small component). Hence, the coupling between the large and small components in (4) and (5) is no longer of great importance, so the main interest becomes the solving of (6) for the large component only. The choice

$$\phi_{II}^{(2)}(0) = \phi_{III}^{(2)}(0), \tag{12}$$

$$\left.\frac{d\phi_{II}^{(2)}}{dx}\right|_{x=0} = \left.\frac{d\phi_{III}^{(2)}}{dx}\right|_{x=0} \tag{13}$$

can now be made for the continuity conditions.

III. BULK RELATIVISTIC KRONIG-PENNEY MODEL

From Bloch's theorem[6]

$$\phi(x) = \mathbf{u}(x)e^{i\mu x} \tag{14}$$

and (8), it follows that

$$\mathbf{u}(x) = \begin{pmatrix}\alpha_1\\ \alpha_2\end{pmatrix} e^{i(\rho_{II}-\mu)x} + \begin{pmatrix}\beta_1\\ \beta_2\end{pmatrix} e^{-i(\rho_{II}+\mu)x}, \tag{15}$$

μ being the wave number. For the KP model,[4] which consists of a linear array of rectangular barriers of height V, width b, and lattice constant $(a+b)$, the continuity conditions for the large component are

$$u_{II}(0) = u_{III}(0), \quad u_{II}(-b) = u_{III}(a), \tag{16}$$

$$u_{II}'(0) = u_{III}'(0), \quad u_{II}'(-b) = u_{III}'(a), \tag{17}$$

where the large component subscript 2 has been dropped for convenience. Substituting (15) into (16) and (17) and solving the resulting determinantal equation for the coefficients gives the relativistic KP (RKP) relation [cf. GD Eq. (46)]

$$\cos\mu(a+b) = \cos\rho_{II}a \cos\rho_{III}b - \sigma \sin\rho_{II}a \sin\rho_{III}b, \tag{18}$$

where

$$\sigma = \tfrac{1}{2}\{\rho_{II}^{-1}+\rho_{III}^{-1}\}. \tag{19}$$

Carrying out the δ-potential transformation, subject to the limiting value [cf. GD Eq. (48)]

$$\lim_{\substack{b\to 0\\ \rho_{III}\to\infty}} \tfrac{1}{2}\rho_{III}^2 ab = -p_R, \tag{20}$$

Eq. (18) simplifies to

$$\cos\mu a = \cos\rho_{II}a + p_R(\sin\rho_{II}a/\rho_{II}a). \tag{21}$$

In the NR limit, (18) and (21) become the familiar KP relation.

[6] F. Bloch, Z. Physik **52**, 555 (1928).

Inserting (15) in (16), using (20) yields

$$\beta_{II} = \lambda_R \alpha_{II}, \tag{22}$$

where

$$\lambda_R = (1-e^{-i(\mu-\rho_{II})a})/(e^{-i(\mu+\rho_{II})a}-1). \tag{23}$$

Hence, because of (14), the large component wave function in the unit cell $0 \leq x \leq a$ is

$$\phi_{II} = \alpha_{II}\{e^{i\rho_{II}x} + \lambda_R e^{-i\rho_{II}x}\}. \tag{24}$$

IV. SURFACE RELATIVISTIC KRONIG-PENNEY MODEL

The surface effect on the KP model is described by terminating the potential at $x=0$ and taking the potential for $x<0$ to be constant (V_I).

A. Energy Expression

In the vacuum region ($x<0$), the large component solution to the Dirac equation is[2,3]

$$\phi_I(x) = \beta e^{i\rho_I x}. \tag{25}$$

At the surface, the continuity conditions are

$$\phi_I(0) = \phi_{II}(0), \quad \phi_I'(0) = \phi_{II}'(0), \tag{26}$$

which lead to

$$\rho_I(1+\lambda_R) = \rho_{II}(1-\lambda_R). \tag{27}$$

From (25) and (27) comes

$$e^{i\mu a} = \cos\xi_{II} + i\xi_I \frac{\sin\xi_{II}}{\xi_{II}}, \tag{28}$$

where

$$\xi_k = \rho_k a. \tag{29}$$

For surface states,[7]

$$\mu = n\pi/a + i\zeta, \quad \zeta \text{ real} > 0 \tag{30}$$

so that (21) becomes

$$(-1)^n \cosh\zeta a = \cos\xi_{II} + p_R \frac{\sin\xi_{II}}{\xi_{II}}. \tag{31}$$

Using (28) and (31) gives the energy expression

$$\xi_{II}\cot\xi_{II} = \{\xi_{II}^2 - \xi_I^2\}/2p_R - i\xi_I, \tag{32}$$

which, in the NR case, reduces to the well-known Tamm relation.[7]

B. Existence Condition

With the aid of (30), subtracting (28) from (31) yields

$$(-1)^n \sinh\mu a = \{p_R - i\xi_I\}\frac{\sin\xi_{II}}{\xi_{II}}. \tag{33}$$

[7] I. Tamm, Z. Physik **76**, 849 (1932).

Since the RKP relation has exactly the same form as the nonrelativistic KP (NRKP) relation, the $(n+1)$th band gap occurs in the range $n\pi \leq \xi_{II} \leq (n+1)\pi$. In any band gap,[8]

$$\operatorname{sign}\left(\frac{\sin\xi_{II}}{\xi_{II}}\right)=(-1)^n, \tag{34}$$

so

$$p_R > i\xi_I \tag{35}$$

from (33). In Tamm's notation,[7]

$$q^2=2m_0a^2V_I/\hbar^2, \quad \xi_0^2=2m_0a^2\epsilon/\hbar^2, \tag{36}$$

hence, (35) becomes

$$p_R > \{q^2-\xi_0^2\}^{1/2}[1-\eta^2\{q^2-\xi_0^2\}]^{1/2} \tag{37}$$

via (7) and (29), with

$$\eta=\hbar/2m_0ac. \tag{38}$$

In the NR limit, (37) reduces to Tamm's condition

$$p > \{q^2-\xi_0^2\}^{1/2}. \tag{39}$$

V. DISCUSSION

In the relativistic formulation, the *upper* band edges are given by

$$\xi_{II}=n\pi, \tag{40}$$

which in a first-order relativistic (IR) approximation becomes[1-3]

$$\xi_0=n\pi-\tfrac{1}{2}\eta^2\xi_0^3. \tag{41}$$

Similarly, the *lower* band edges are given by [cf. (37)]

$$p_R^2=\{q^2-\xi_0^2\}[1-\eta^2\{q^2-\xi_0^2\}]. \tag{42}$$

The η^2 terms in (41) and (42) are the IR corrections to the NR band edges. The effect of these terms is to *shift* the band edges towards the center of the energy spectrum, i.e., to band-structure diagram *shrinks*, in agreement with the numerical calculations of GD.

Solutions of (32) *always* exist in the range $n\pi < \xi_{II} < (n+1)\pi$, provided $n \neq 0$. For these solutions to represent surface states, they must also satisfy the inequality (37). When $n=0$, (32) has solutions only if

$$\text{right-hand side}\,|_{\xi_{II}=0} > 1. \tag{43}$$

Thus, for surface states to occur in the first band gap, *both* (37) and (43) must be fulfilled.

The inequality (37) can be written

$$p_R^2-\{q^2-\xi_0^2\} > -\eta^2\{q^2-\xi_0^2\}^2. \tag{44}$$

When the left-hand side is *positive*, i.e.,

$$p_R^2 > \{q^2-\xi_0^2\}, \tag{45}$$

(44) is always satisfied, since the right-hand side is always negative. Because (45) is analogous to the NR Tamm condition (40), the surface state satisfying it is called a relativistic Tamm state (RTS). In addition, it is also possible for (45) to be satisfied when the left-hand side is *negative*, i.e., when (45) is violated. Since such a possibility arises only as a result of the Dirac formulation, the surface state satisfying

$$0 > p_R^2-\{q^2-\xi_0^2\} > -\eta^2\{q^2-\xi_0^2\}^2 \tag{46}$$

is known as a Dirac surface state (DSS).

The classification of surface states, for heavy atomic solids, into RTS and DSS was first used in a previous paper.[2] However, contrary to that work, where *both* components of the spinor were considered, the present treatment is concerned with the *large* component only. In this way, a much simpler analysis was possible, without any loss of the relativistic effect in solid state physics.

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APPENDIX

Although the present approximate treatment leads to the same qualitative results as the previous accurate calculations,[2] it is useful to estimate the order of the error introduced by this approximation.

In this paper, the small component is replaced by the derivative of the large component, so, as can be seen from (8) and (9), the ratio ρ_{II}/ρ_I is used instead of γ_{II}/γ_I in the matching condition. Such an interchange of ρ's and γ's also occurs in the KP relation (18) and surface-energy expression (27).

From (10) and (7) comes

$$\gamma_{II}/\gamma_I=(\rho_{II}/\rho_I)(1-V_1/\epsilon+2m_0c^2),$$

thus, the fractional error introduced by the approximation is

$$V_1/(\epsilon+2m_0c^2)\sim v^2/c^2$$

for $V_1 \sim \epsilon$. Equation (41) shows that the relativistic correction to the energy is

$$\tfrac{1}{2}\eta^2\xi_0^3\sim v^3/c^2.$$

Hence, the ratio of the error to the relativistic correction is $O(v^{-1})$. When $n>8$, $O(v^{-1})<10^{-1}$, and for higher band numbers, where the relativistic effect is more pronounced, the approximation becomes even better.

[8] M. Stęślicka, Physica (to be published).