Relativistic Green's-function method for solids and molecules*

Augusto Agostinho Neto and Luiz G. Ferreira
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, São Paulo, Brazil
(Received 11 December 1975)

The relativistic multiple-scattering method (Green's-function method) for crystals and molecules is developed from the definition of the four-component wave function in the two regions. The secular equation is obtained by matching the wave functions at the two sides of the sphere surface separating the two regions. The secular equation is expanded in powers of $1/c^2$ so as to exhibit the mass and spin-orbit corrections. As an application of the method we present the results for the band structure of lead.

I. INTRODUCTION

In this paper we present a systematic derivation of the relativistic multiple-scattering method for solids and molecules (Green's-function method, Korringa-Kohn-Rostoker method). This paper is preceded by the works of Ref. 1–8 dealing with the same subject. Thus we avoid repeating their results and put emphasis in those aspects of the problem which have not yet received special attention in the literature. Our derivation, instead of starting by postulating a relativistic Green's-function, follows the safer route of the definition of the four-component wave function, both inside and outside the spheres circumscribing the atoms. Thus we attain to obtain the wave function in a simple and precise way, a result yet unpublished in the literature. To obtain a secular equation we just match the wave functions inside and outside at the sphere surface. Then, this secular equation is expanded in a power series of $1/c^2$ so as to make explicit the mass correction and the spin-orbit interaction. The derivation is truly made for solids but the final secular equation is put in such a form that its modification for molecules becomes a very simple matter.

As an application of the method, we made the band-structure calculation for lead. Lead being a very heavy element, we could make the band calculation non-self-consistent. We found that the bands of lead have important contributions from higher angular momenta such as $l=2$ and 3.

II. THEORY

We subdivide the crystal unit cell into two regions: region I is the space inside the sphere circumscribing the atom; region II is the space outside the sphere. In region I the potential is spherically symmetrical, and in region II a constant.

A. Trial function for region I

${}^{\mathrm{I}}\psi$, trial function for region I, will be constructed as a linear superposition of basis functions ${}^{\mathrm{I}}\phi_{\kappa,\mu}$

$$ {}^{\mathrm{I}}\psi = \sum_{\kappa,\mu} a_{\kappa,\mu}\, {}^{\mathrm{I}}\phi_{\kappa,\mu}, \tag{1} $$

where $a_{\kappa,\mu}$ are constant coefficients and ${}^{\mathrm{I}}\phi_{\kappa,\mu}$ is such that

$$ H\,{}^{\mathrm{I}}\phi_{\kappa,\mu} = \epsilon\,{}^{\mathrm{I}}\phi_{\kappa,\mu}, \tag{2} $$

where H stands for the Dirac Hamiltonian. In the standard representation

$$ H = \beta mc^2 + c\vec{\alpha}\cdot\vec{\mathrm{p}} + V(\vec{\mathrm{r}}), \tag{3} $$

where $\vec{\alpha}$ and β are the usual 4×4 matrices.

Since the potential in region I is spherically symmetrical a judicious choice for ${}^{\mathrm{I}}\phi_{\kappa,\mu}$ is

$$ {}^{\mathrm{I}}\phi_{\kappa,\mu} = \begin{pmatrix} f_\kappa(r)\chi_{\kappa,\mu}(\hat{r},\sigma) \\ i\tilde{f}_{-\kappa}(r)\chi_{-\kappa,\mu}(\hat{r},\sigma) \end{pmatrix}, \tag{4} $$

where $\chi_{\kappa,\mu}(\hat{r},\sigma)$ are the usual spherical spinors, and f_κ and $\tilde{f}_{-\kappa}$ satisfy the radial equations[9]

$$ (rf_\kappa)' + (\kappa/r)(rf_\kappa) - (1/\hbar c)[\epsilon + mc^2 - V(r)]r\tilde{f}_{-\kappa} = 0, \tag{5a} $$

$$ (r\tilde{f}_{-\kappa})' - (\kappa/r)(r\tilde{f}_{-\kappa}) + (1/\hbar c)[\epsilon - mc^2 - V(r)]rf_\kappa = 0. \tag{5b} $$

The spherical spinors are superpositions of direct products between angular and spin functions, namely

$$ \chi_{\kappa,\mu}(\hat{r},\sigma) = \sum_{l,m,\sigma'} (\kappa,\mu\,|\,l,m,\sigma')Y_l^m(\hat{r})\chi^{\sigma'}(\sigma), \tag{6} $$

where $Y_l^m(r)$ stands for the usual spherical harmonic function, and $\chi^{\sigma'}(\sigma)$ specifies the spin function,

$$ \chi^{\sigma'}(\sigma) = \delta_{\sigma',\sigma}. \tag{7} $$

The symbols

$$ (\kappa,\mu\,|\,l,m,\sigma) = \delta_{l,L(\kappa)}\delta_{m+\sigma,\mu}C(l,\tfrac{1}{2},j;\mu-\sigma,\sigma), \tag{8} $$

with

$$ L(\kappa) = |\kappa| + \tfrac{1}{2}(S_\kappa - 1), \tag{9a} $$

$$S_\kappa = \kappa/|\kappa|, \tag{9b}$$

$$j = |\kappa| - \tfrac{1}{2}, \tag{9c}$$

and the $C(l, \frac{1}{2}, j; \mu - \sigma, \sigma)$ denoting the Clebsch-Gordan coefficients for the addition of angular functions in the notation of Ref. 9, are very useful tools for changing the representation κ, μ into l, m, σ, and vice versa, and will be frequently used in the following. Using these coefficients we can also write

$$Y_l^m(\hat{r})\chi^\sigma(\sigma') = \sum_{\kappa,\mu} (\kappa, \mu | l, m, \sigma)\chi_{\kappa,\mu}(\hat{r}, \sigma'). \tag{10}$$

From the relation above and the relation (6) we obtain the properties

$$\sum_{l,m,\sigma} (\kappa, \mu | l, m, \sigma)(\kappa', \mu' | l, m, \sigma) = \delta_{\kappa,\kappa'}\delta_{\mu,\mu'} \tag{11}$$

and

$$\sum_{\kappa,\mu} (\kappa, \mu | l, m, \sigma)(\kappa, \mu | l', m', \sigma') = \delta_{l,l'}\delta_{m,m'}\delta_{\sigma,\sigma'} . \tag{12}$$

Equations (1), (4), and (5) define completely the trial function ${}^{\mathrm{I}}\psi$ inside region I, for a given value of the energy ϵ

$${}^{\mathrm{I}}\psi = \sum_{\kappa,\mu} a_{\kappa,\mu} \begin{pmatrix} f_\kappa(r)\chi_{\kappa,\mu}(\hat{r}, \sigma) \\ i\tilde{f}_{-\kappa}(r)\chi_{-\kappa,\mu}(\hat{r}, \sigma) \end{pmatrix}. \tag{13}$$

B. Trial function for region II

We write ${}^{\mathrm{II}}\psi$ in the form

$${}^{\mathrm{II}}\psi = \sum_{\kappa,\mu} b_{\kappa,\mu}\, {}^{\mathrm{II}}\phi_{\kappa,\mu,\vec{k}}(\vec{r}, \sigma) , \tag{14}$$

with

$${}^{\mathrm{II}}\phi_{\kappa,\mu,\vec{k}}(\vec{r}, \sigma) = \sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}}\, {}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r} - \vec{l}, \sigma) , \tag{15}$$

where the sum is over all the lattice vectors. ${}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r}, \sigma)$ is such that

$$(\beta mc^2 + c\vec{\alpha}\cdot\vec{p} + \bar{V})\, {}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r}, \sigma) = \epsilon\, {}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r}, \sigma) , \tag{16}$$

where $\bar{V}$ is the value for the potential in region II.

From (16) and repeating the steps of Sec. I, we obtain

$${}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r}, \sigma') = \begin{pmatrix} v_\kappa(Kr)\chi_{\kappa,\mu}(\hat{r}, \sigma') \\ i\tilde{v}_{-\kappa}(Kr)\chi_{-\kappa,\mu}(\hat{r}, \sigma') \end{pmatrix}. \tag{17}$$

In the case of $\epsilon - \bar{V} > mc^2$, v_κ are spherical Bessel functions of the second kind[10]

$$v_\kappa(Kr) = y_{L(\kappa)}(Kr) , \tag{18a}$$

$$\tilde{v}_{-\sigma}(Kr) = \xi_{-\kappa}v_{-\kappa}(Kr) = -\frac{\hbar cKS_{-\kappa}}{\epsilon + mc^2 - \bar{V}}\, v_{-\kappa}(Kr) = \frac{\hbar c}{\epsilon + mc^2 - \bar{V}} \left(Kv'_\kappa(Kr) + \frac{\kappa + 1}{r} v_\kappa(Kr) \right), \tag{18b}$$

and

$$K^2 = [(\epsilon - \bar{V})^2 - m^2c^4]/\hbar^2c^2 . \tag{19}$$

In what follows we shall also use the following set of symbols:

$$u_\kappa(Kr) = j_{L(\kappa)}(Kr) \quad \text{(Bessel of 1st kind)} \tag{20a}$$

and

$$\tilde{u}_{-\kappa}(Kr) = \xi_{-\kappa}u_{-\kappa}(Kr) , \tag{20b}$$

analogously to Eq. (18b).

C. Structure constants

In this section we show how to perform the sum

$${}^{\mathrm{II}}\phi_{\kappa,\mu,\vec{k}}(\vec{r}, \sigma) = \sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}}\, {}^{\mathrm{II}}\phi_{\kappa,\mu}(\vec{r} - \vec{l}, \sigma) . \tag{21}$$

The derivation will be done just for the case $\epsilon - \bar{V} > mc^2$. We begin from the well-known relations:

$$y_0(K|\vec{r} - \vec{l}|) = 4\pi \sum_{l,m} j_l(Kr)\, y_l(K|\vec{l}|) Y_l^m(\hat{r}) Y_l^{m*}(\hat{l}) \tag{22}$$

and

$$Y_l^m(\hat{l})\, y_l(K|\vec{l}|) = (-i)^l Y_l^m(\nabla_{\vec{l}}/iK)\, y_0(K|\vec{l}|) . \tag{23}$$

The two relations above will be written in a more useful form.

Let us consider the sum

$$\sum_{\substack{\kappa,\mu \\ \text{fixed } l}} \chi^*_{\kappa,\mu}(\hat{r}', \sigma')\chi_{\kappa,\mu}(\hat{r}, \sigma) = \sum_{\substack{\kappa,\mu \\ \text{fixed } l}} \langle \hat{r}, \sigma | \kappa, \mu \rangle \langle \kappa, \mu | \hat{r}', \sigma' \rangle = \sum_{m,\Sigma} \langle \hat{r}, \sigma | l, m, \Sigma \rangle \langle l, m, \Sigma | \hat{r}', \sigma' \rangle$$

$$= \sum_{m,\Sigma} \delta_{\Sigma,\sigma}\delta_{\Sigma,\sigma'} Y_l^m(\hat{r}) Y_l^m(\hat{r}')^* = \delta_{\sigma,\sigma'} \sum_m Y_l^m(\hat{r}) Y_l^m(\hat{r}')^* . \tag{24}$$

Using (24), (22) changes into

$$y_0(K|\vec{r}-\vec{l}|)\delta_{\sigma,\sigma'}=4\pi\sum_{\kappa,\mu}u_\kappa(Kr)v_\kappa(K|\vec{l}|)\chi^*_{\kappa,\mu}(\hat{l},\sigma)\chi_{\kappa,\mu}(\hat{r},\sigma') \ . \tag{25}$$

Using the relation (6), we also write (23) as

$$\chi_{\kappa,\mu}(\hat{l},\sigma)v_\kappa(K|\vec{l}|)=(-i)^{L(\kappa)}\chi_{\kappa,\mu}(\nabla_{\vec{l}}/iK,\sigma)\,y_0(K|\vec{l}|) \ . \tag{26}$$

The sum (21) is split into two parts: one part consisting only of the $\vec{l}=0$ term. Using the relation (26) with $\nabla_{\vec{r}-\vec{l}}=-\nabla_{\vec{l}}$ and the property $\chi_{\kappa,\mu}(-\hat{l},\sigma)=(-1)^{L(\kappa)}\chi_{\kappa,\mu}(\hat{l},\sigma)$ we write

$$\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}\,\mathrm{II}\phi_{\kappa,\mu}(\vec{r}-\vec{l},\sigma)=\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}\begin{pmatrix}v_\kappa(K|\vec{r}-\vec{l}|)\chi_{\kappa,\mu}(\vec{r}-\vec{l},\sigma)\\ i\xi_{-\kappa}v_{-\kappa}(K|\vec{r}-\vec{l}|)\chi_{-\kappa,\mu}(\vec{r}-\vec{l},\sigma)\end{pmatrix}$$

$$=\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}\begin{pmatrix}i^{L(\kappa)}\chi_{\kappa,\mu}(\nabla_{\vec{l}}/i\hat{K},\sigma)\,y_0(K|\vec{r}-\vec{l}\,|)\\ i^{L(-\kappa)+1}\xi_{-\kappa}\chi_{-\kappa,\mu}(\nabla_{\vec{l}}/iK,\mu)\,y_0(K|\vec{r}-\vec{l}|)\end{pmatrix}. \tag{27}$$

The great component in Eq. (27) can be written

$$\sum_{\substack{\vec{l}\neq 0\\ \sigma'}}e^{i\vec{k}\cdot\vec{l}}i^{L(\kappa)}\chi_{\kappa,\mu}(\nabla_{\vec{l}}/iK,\sigma')\,y_0(K|\vec{r}-\vec{l}|)\delta_{\sigma\sigma'}$$

$$=4\pi\sum_{\substack{\vec{l}\neq 0\\ \sigma',\kappa',\mu'}}e^{i\vec{k}\cdot\vec{l}}i^{L(\kappa)-L(\kappa')}\chi_{\kappa,\mu}(\nabla_{\vec{l}}/iK,\sigma')\chi^\dagger_{\kappa',\mu'}(\nabla_{\vec{l}}/iK,\sigma')\,y_0(K|\vec{l}|)u_{\kappa'}(Kr)\chi_{\kappa',\mu'}(\hat{r},\sigma) \ . \tag{28}$$

Now

$$\sum_{\sigma'}\chi^\dagger_{\kappa',\mu'}(\nabla_{\vec{l}}/iK,\sigma')\chi_{\kappa,\mu}(\nabla_{\vec{l}}/iK,\sigma')=\sum_{\substack{l,m,\Sigma\\ l',m',\Sigma'\\ \sigma'}}(\kappa',\mu'|l',m',\Sigma')(\kappa,\mu|l,m,\Sigma)Y^{m'\dagger}_{l'}(\nabla_{\vec{l}}/iK)Y^m_l(\nabla_{\vec{l}}/iK)\delta_{\sigma',\Sigma}\delta_{\sigma',\Sigma'} \ . \tag{29}$$

The product of spherical harmonics can be written

$$Y^{m'\dagger}_{l'}(\nabla_{\vec{l}}/iK)Y^m_l(\nabla_{\vec{l}}/iK)=\sum_{L,M}\langle l',m'|Y^{M*}_L|l,m\rangle Y^M_L(\nabla_{\vec{l}}/iK), \tag{30}$$

where $\langle l',m'|Y^{M*}_L|l,m\rangle$ are Gaunt integrals. Using (23) and defining

$$D_{L,M}(\vec{k},K)=\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}Y_L(K|\vec{l}|)Y^M_L(\hat{l}) \tag{31}$$

in a similar way as done by Kohn and Rostocker,[11] and also

$$G_{l',m';l,m}(\vec{k},K)=4\pi\sum_{L,M}i^{l+L-l'}\langle l',m'|Y^{M*}_L|l,m\rangle D_{L,M}, \tag{32}$$

we have for the sum for the great component

$$\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}v_\kappa(K|\vec{r}-\vec{l}|)\chi_{\kappa,\mu}(\vec{r}-\vec{l},\sigma)=\sum_{\substack{\kappa',\mu'\\ l,m,\Sigma\\ l',m',\Sigma'}}(\kappa',\mu'|l',m',\Sigma')G_{l',m';l,m}\delta_{\Sigma,\Sigma'}(\kappa,\mu|l,m,\Sigma)u_{\kappa'}(Kr)\chi_{\kappa',\mu'}(\hat{r},\sigma)$$

$$=\sum_{\kappa',\mu'}B_{\kappa',\mu';\kappa,\mu}(\vec{k},K)u_{\kappa'}(Kr)\chi_{\kappa',\mu'}(\hat{r},\sigma), \tag{33}$$

with

$$B_{\kappa'\mu';\kappa,\mu}=\sum_{\substack{l,m,\Sigma\\ l',m',\Sigma'}}(\kappa',\mu'|l',m',\Sigma')G_{l',m';l,m}\delta_{\Sigma',\Sigma}(\kappa,\mu|l,m,\Sigma). \tag{34}$$

For the small component in Eq. (27) it is sufficient to change κ into $-\kappa$, or

$$i\sum_{\vec{l}\neq 0} e^{i\vec{k}\cdot\vec{l}}\tilde{v}_{-\kappa}(K|\vec{r}-\vec{l}|)\chi_{-\kappa,\mu}(\vec{r}-\vec{l},\sigma)=i\sum_{\kappa',\mu'}\frac{\xi_{-\kappa}}{\xi_{-\kappa'}}B_{-\kappa',\mu';-\kappa,\mu}\tilde{u}_{-\kappa'}(Kr)\chi_{-\kappa',\mu'}(\hat{r},\sigma), \tag{35a}$$

where

$$\xi_{-\kappa}/\xi_{-\kappa'}=S_\kappa S_{\kappa'}. \tag{35b}$$

On the other hand,[9]

$$\chi_{-\kappa,\mu}(\hat{r},\sigma)=-\vec{\sigma}\cdot\hat{r}\chi_{\kappa,\mu}(\hat{r},\sigma). \tag{36}$$

Thus

$$\begin{aligned}(-\kappa,\mu\,|l,m,\sigma)&=-\sum_{l'',m'',\sigma''}(\kappa,\mu\,|l'',m'',\sigma'')\langle l,m,\sigma|\vec{\sigma}\cdot\hat{r}|l'',m'',\sigma''\rangle\\&=-\sum_{l'',m'',\sigma''}\langle l,m,\sigma|\vec{\sigma}\cdot\hat{r}|l'',m'',\sigma''\rangle\langle l'',m'',\sigma''\,|\kappa,\mu\rangle.\end{aligned} \tag{37}$$

Defining the Hermitian operator G such that

$$\delta_{\Sigma,\Sigma'}G_{l',m';l,m}=i^{l-l'}\langle l',m',\Sigma'|G|l,m,\Sigma\rangle \tag{38}$$

or

$$G=4\pi\sum_{L,M}i^L D_{L,M}Y_L^{M*}(\hat{r}), \tag{39}$$

we have

$$\frac{\xi_{-\kappa}}{\xi_{-\kappa'}}B_{-\kappa',\mu';-\kappa,\mu}=\sum_{\substack{l',m',\Sigma'\\l,m,\Sigma}}S_\kappa S_{\kappa'}i^{L(-\kappa)-L(-\kappa')}(-\kappa',\mu'|l',m',\Sigma')\langle l',m',\Sigma'|G|l,m,\Sigma\rangle(-\kappa,\mu\,|l,m,\Sigma), \tag{40}$$

but from (9a)

$$S_\kappa S_{\kappa'}i^{L(-\kappa)-L(-\kappa')}=i^{L(\kappa)-L(\kappa')}, \tag{41}$$

(40) becomes

$$\begin{aligned}&\sum_{\substack{l',m',\Sigma'\\l,m,\Sigma\\l'',m'',\Sigma''\\l''',m''',\Sigma'''}}i^{L(\kappa)-L(\kappa')}\langle\kappa',\mu'|l'',m'',\Sigma''\rangle\langle l'',m'',\Sigma''|\vec{\sigma}\cdot\hat{r}|l',m',\Sigma'\rangle\\&\times\langle l',m',\Sigma'|G|l,m,\Sigma\rangle\langle l,m,\Sigma|\vec{\sigma}\cdot\hat{r}|l''',m''',\Sigma'''\rangle\langle l''',m''',\Sigma'''|\kappa,\mu\rangle\\&=\sum_{\substack{l',m',\Sigma'\\l,m,\Sigma}}(\kappa',\mu'|l',m',\Sigma')G_{l',m';l,m}\delta_{\Sigma',\Sigma}(\kappa,\mu\,|l,m,\sigma)=B_{\kappa',\mu';\kappa,\mu}.\end{aligned} \tag{42}$$

Finally, for the small component we have the form

$$i\sum_{\vec{l}\neq 0}e^{i\vec{k}\cdot\vec{l}}\tilde{v}_{-\kappa}(K|\vec{r}-\vec{l}|)\chi_{-\kappa,\mu}(\vec{r}-\vec{l},\sigma)=i\sum_{\kappa',\mu'}B_{\kappa',\mu';\kappa,\mu}\tilde{u}_{-\kappa'}(Kr)\chi_{-\kappa',\mu'}(\hat{r},\sigma). \tag{43}$$

In this way we have the following form for the trial function in the region II, for the case $\epsilon-V>mc^2$

$${}^{II}\psi(\vec{r},\sigma)=\sum_{\kappa,\mu}b_{\kappa,\mu}\left[\begin{pmatrix}v_\kappa(Kr)\chi_{\kappa,\mu}(\hat{r},\sigma)\\ i\tilde{v}_{-\kappa}(Kr)\chi_{-\kappa,\mu}(\hat{r},\sigma)\end{pmatrix}+\sum_{\kappa',\mu'}B_{\kappa',\mu';\kappa,\mu}\begin{pmatrix}u_{\kappa'}(Kr)\chi_{\kappa,\mu}(\hat{r},\sigma)\\ i\tilde{u}_{-\kappa',\mu'}(\hat{r},\sigma)\end{pmatrix}\right]. \tag{44}$$

III. SECULAR EQUATION

A. Standard forms for crystals

In order to obtain a secular equation we have just to equate the great and small components of (13) and (44) at the sphere surface. Letting R be the radius of the sphere, we obtain

$$a_{\kappa,\mu}f_\kappa(R)=b_{\kappa,\mu}v_\kappa(KR)+u_\kappa(KR)\sum_{\kappa',\mu'}B_{\kappa,\mu;\kappa',\mu'}b_{\kappa',\mu'}, \tag{45}$$

$$a_{\kappa,\mu}f_{-\kappa}(R)=b_{\kappa,\mu}\tilde{v}_{-\kappa}(KR)+\tilde{u}_{-\kappa}(KR)\sum_{\kappa',\mu'}B_{\kappa,\mu;\kappa',\mu'}b_{\kappa',\mu'}. \tag{46}$$

From the equation above we can obtain by a very simple algebra the secular equation in the form

$$\frac{v_\kappa(KR)\tilde{f}_{-\kappa}(R)-\tilde{v}_{-\kappa}(KR)f_\kappa(R)}{u_\kappa(KR)\tilde{f}_{-\kappa}(R)-\tilde{u}_{-\kappa}(KR)f_\kappa(R)}b_{\kappa,\mu}+\sum_{\kappa',\mu'}B_{\kappa,\mu;\kappa',\mu'}b_{\kappa',\mu'}=0, \quad (47)$$

which is equal to what has been published elsewhere,[1,2] and

$$a_{\kappa,\mu}=\frac{\tilde{u}_{-\kappa}(KR)v_\kappa(KR)-u_\kappa(KR)\tilde{v}_{-\kappa}(KR)}{\tilde{u}_{-\kappa}(KR)f_\kappa(R)-u_\kappa(KR)\tilde{f}_{-\kappa}(R)}b_{\kappa,\mu}, \quad (48)$$

which relates the coefficients of the expansion in region I to those of region II. This relation permits us to normalize the wave function, as shown in Ref. 12.

The secular equation (47) can be cast in a more useful form by defining the symbols

$$b^\sigma_{l,m}=\sum_{\kappa,\mu}(\kappa,\mu\,|\,l,m,\sigma)b_{\kappa,\mu} \quad (49a)$$

and

$$b_{\kappa,\mu}=\sum_{l,m,\kappa}(\kappa,\mu\,|\,l,m,\sigma)b^\sigma_{l,m}. \quad (49b)$$

Recalling Eq. (34) and using the orthogonality given by Eq. (12), we arrive at

$$\sum_{\substack{\kappa,\mu\\ l',m',\sigma'}}(\kappa,\mu\,|\,l,m,\sigma)t^{-1}_\kappa(\kappa,\mu\,|\,l',m',\sigma')b^{\sigma'}_{l',m'}+\sum_{l',m',\sigma'}G_{l,m;l',m'}\delta_{\sigma,\sigma'}b^{\sigma'}_{l',m'}=0, \quad (50)$$

where

$$t^{-1}_\kappa=\frac{v_\kappa(KR)\tilde{f}_{-\kappa}(R)-\tilde{v}_{-\kappa}(KR)f_\kappa(R)}{u_\kappa(KR)\tilde{f}_{-\kappa}(R)-\tilde{u}_{-\kappa}(KR)f_\kappa(R)}. \quad (51)$$

B. Limit of $c=\infty$

In this limit, from Eq. (5a) we obtain

$$\tilde{f}_{-\kappa}=(\hbar/2mc)\{f'_\kappa+[(\kappa+1)/r]f_\kappa\}, \quad (52a)$$

TABLE I. Potential for lead in atomic units (rydberg).

r	$rV(r)$	r	$rV(r)$
1.2169×10^{-4}	-1.6388×10^{2}	2.2058×10^{-2}	-1.4303×10^{2}
1.4863×10^{-4}	-1.6385×10^{2}	2.6943×10^{-2}	-1.3929×10^{2}
1.8154×10^{-4}	-1.6382×10^{2}	3.2908×10^{-2}	-1.3500×10^{2}
2.2173×10^{-4}	-1.6377×10^{2}	4.0194×10^{-2}	-1.3013×10^{2}
2.7082×10^{-4}	-1.6372×10^{2}	4.9093×10^{-2}	-1.2465×10^{2}
3.3078×10^{-4}	-1.6365×10^{2}	5.9962×10^{-2}	-1.1852×10^{2}
4.0402×10^{-4}	-1.6357×10^{2}	7.3237×10^{-2}	-1.1176×10^{2}
4.9347×10^{-4}	-1.6347×10^{2}	8.9452×10^{-2}	-1.0437×10^{2}
6.0273×10^{-4}	-1.6335×10^{2}	1.0926×10^{-1}	-9.6412×10
7.3617×10^{-4}	-1.6321×10^{2}	1.3345×10^{-1}	-8.7956×10
8.9916×10^{-4}	-1.6303×10^{2}	1.6299×10^{-1}	-7.9153×10
1.0982×10^{-3}	-1.6280×10^{2}	1.9908×10^{-1}	-7.0129×10
1.3414×10^{-3}	-1.6253×10^{2}	$2.431\,56\times10^{-1}$	-6.0976×10
1.6384×10^{-3}	-1.6220×10^{2}	2.9699×10^{-1}	-5.1864×10
2.0011×10^{-3}	-1.6180×10^{2}	3.6274×10^{-1}	-4.3065×10
2.4442×10^{-3}	-1.6130×10^{2}	4.4306×10^{-1}	-3.5065×10
2.9853×10^{-3}	-1.6070×10^{2}	5.4116×10^{-1}	-2.8140×10
3.6463×10^{-3}	-1.5998×10^{2}	6.6097×10^{-1}	-2.2220×10
4.4536×10^{-3}	-1.5910×10^{2}	8.0731×10^{-1}	-1.7179×10
5.4396×10^{-3}	-1.5806×10^{2}	9.8605×10^{-1}	-1.2935×10
6.6439×10^{-3}	-1.5681×10^{2}	1.2044	-9.5113
8.1149×10^{-3}	-1.5532×10^{2}	1.4710	-6.9205
9.9116×10^{-3}	-1.5357×10^{2}	1.7967	-5.0587
1.2106×10^{-2}	-1.5151×10^{2}	2.1945	-3.7923
1.4786×10^{-2}	-1.4910×10^{2}	2.6806	-3.0295
1.8060×10^{-2}	-1.4628×10^{2}	3.2738	-2.8231

$$\tilde{v}_{-\kappa}=(\hbar/2mc)\{Kv'_\kappa+[(\kappa+1)/r]v_\kappa\}, \quad (52b)$$

$$\tilde{u}_{-\kappa}=(\hbar/2mc)\{Ku'_\kappa+[(\kappa+1)/r]u_\kappa\}. \quad (52c)$$

Then

$$t^{-1}_\kappa=\frac{v_\kappa(KR)f'_\kappa(R)-Kv'_\kappa(KR)f_\kappa(R)}{u_\kappa(KR)f'_\kappa(R)-Ku'_\kappa(KR)f_\kappa(R)}=t^{-1}_{L(\kappa)}, \quad (53)$$

where

$$t^{-1}_l=\frac{y_l(KR)f'_l(R)-Ky'_l(KR)f_l(R)}{j_l(KR)f'_l(R)-Kj'_l(KR)f_l(R)}, \quad (54)$$

TABLE II. Eigenvalues (rydbergs) at point K as function of the secular matrix size.

Level \ Dimension of secular matrix	2	4	8	12	18	24	32
1	-0.800	-0.800	-0.800	-0.818	-0.810	-0.822	-0.820
2	•••	-0.590	-0.610	-0.638	-0.629	-0.629	-0.630
3	•••	•••	-0.483	-0.427	-0.488	-0.540	-0.540
4	•••	•••	-0.268	-0.246	-0.224	-0.250	-0.217

TABLE III. Eigenvalues (rydbergs) at point W as function of the secular matrix size.

Level \ Dimension of secular matrix	2	4	8	12	18	24	32
1	−0.763	−0.763	−0.763	−0.724	−0.724	−0.802	−0.806
2	•••	−0.580	−0.565	−0.610	−0.613	−0.570	−0.589
3	•••	•••	•••	•••	•••	−0.310	−0.267
4	•••	−0.220	−0.220	•••	•••	−0.290	−0.244

because of Eqs. (18a) and (20a), and because the solution of Eq. (5) reduces to the solution of the Schrödinger equation, $f_l(r)$. Then, the first term in Eq. (50) becomes

$$\sum_{\substack{\kappa,\mu\\ l',m',\sigma'}} t_l^{-1}(\kappa,\mu\,|\,l,m,\sigma)(\kappa,\mu\,|\,l',m',\sigma')b^{\sigma'}_{l',m'} = t_l^{-1}b^{\sigma}_{l,m}, \tag{55}$$

because of the orthogonality relation (12). Thus Eq. (50) becomes the standard Korringa-Kohn-Rostoker secular equation for a nonrelativistic electron.

C. Case of molecules

The multiple-scattering method for molecules differs from the version for crystals (Korringa-Kohn-Rostoker method) in just one respect: it is simpler because one does not become involved with the complicate lattice sums. In the present, case, though, the derivation was made for a crystal with just one atom per cell. In modifying Eq. (50) to situations with many atomic species, one must add extra subscripts to account for the many atoms. This is a simple generalization and it is of no use repeating all the steps leading to the secular equation. As written in the form of Eq. (50), the secular equation can be readily generalized to

$$\sum_{\substack{\kappa,\mu\\ l',m',\sigma'}} (\kappa,\mu\,|\,l,m,\sigma)t^{-1}_{p,\kappa}(\kappa,\mu\,|\,l',m',\sigma')b^{\sigma'}_{p,l',m'} + \sum_{p',l',m',\sigma'} G_{p,l,m;p',l',m'}\delta_{\sigma,\sigma'}b^{\sigma'}_{p',l',m'} = 0, \tag{56}$$

where the symbols have their usual meaning.

D. Relativistic corrections up to the order $1/c^2$

In many instances one does not want full relativistic treatment of Eq. (50), but just an expansion up to terms of order $1/c^2$. Thus we consider this expansion of t_κ^{-1} in Eq. (50). In what follows, we shall omit the subscript κ unless it is strictly necessary. Defining

$$w = \epsilon - mc^2, \tag{57}$$

$$p = rf_\kappa \equiv rf, \tag{58}$$

$$q = \hbar c r\bar{f}_{-\kappa} \equiv \hbar c r\bar{f}, \tag{59}$$

we write Eqs. (5) as

$$p' + \frac{\kappa}{r}p - \frac{1}{\hbar^2}\left(2m + \frac{w - V(r)}{c^2}\right)q = 0, \tag{60a}$$

$$q' - (\kappa/r)q + [w - V(r)]p = 0. \tag{60b}$$

In the limit $c = \infty$, corresponding to Eqs. (60) we have the following equations for p_0 and q_0:

$$p_0' + (\kappa/r)p_0 - (2m/\hbar^2)q_0 = 0, \tag{61a}$$

$$q_0' - (\kappa/r)q_0 + [w - V(r)]p_0 = 0. \tag{61b}$$

In the following, the subscript 0 implies the limit $c = \infty$. Multiplying Eq. (60a) by q_0, Eq. (60b) by $-p_0$, Eq. (61a) by $-q$, and Eq. (61b) by p, and summing

$$\frac{d}{dr}(q_0p - qp_0) = \frac{w - V(r)}{\hbar^2c^2}q_0q. \tag{62}$$

Integrating

$$\frac{q(R)}{p(R)} = \frac{q_0(R)}{p_0(R)} - \frac{1}{p_0(R)p(R)}\int_0^R \frac{w - V(r)}{\hbar^2c^2}q_0(r)q(r)\,dr.$$

Up to the order $1/c^2$, the equation above is equivalent to

TABLE IV. Eigenvalues (rydbergs) at the symmetry points.

Γ	−1.2225			
W	−0.8061	−0.5890	−0.2667	−0.2440
X	−0.8200	−0.5257	−0.3243	
K	−0.8200	−0.6300	−0.5400	−0.2167
L	−0.9300	−0.7800		

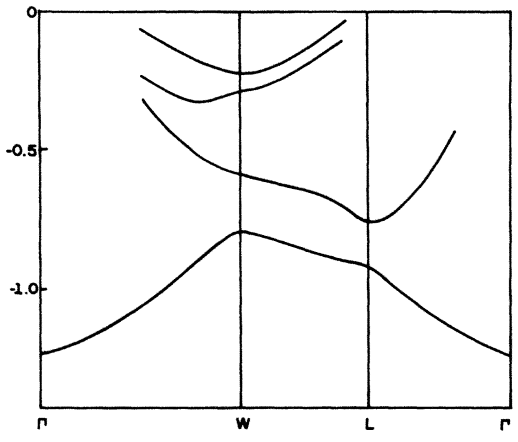

FIG. 1. Band structure of lead calculated by the present method.

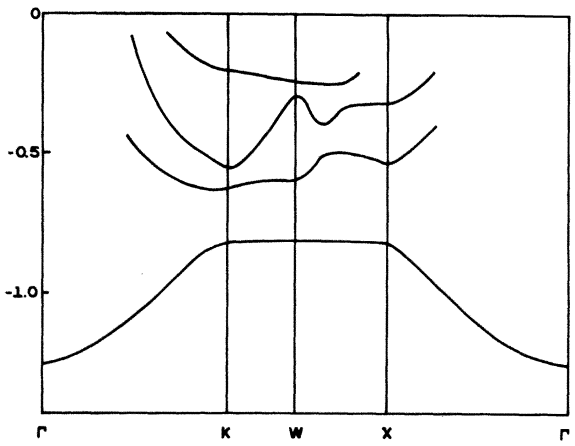

FIG. 3. Band structure of lead calculated by the present method.

$$\hbar c\frac{\tilde{f}}{f}=\hbar c\frac{\tilde{f}_0}{f_0}-\frac{1}{R^2f_0(R)^2}\int_0^R[w-V(r)]r^2\tilde{f}_0(r)^2\,dr. \tag{63}$$

Then we define the symbols

$$F=\tilde{f}/f, \tag{64a}$$

$$V=\tilde{v}/v, \tag{64b}$$

$$U=\tilde{u}/u, \tag{64c}$$

and the symbols F_0, V_0, U_0, these ratios when K^2 is held fixed and $c=\infty$. Since in this limit, K^2 is fixed,

$$v=v_0, \quad u=u_0,$$

but that is not the case of $\tilde{v}$, $\tilde{u}$, f, and $\tilde{f}$. From (63) one has

$$F=F_0-\frac{1}{\hbar cR^2f_0(R)^2}\int_0^R[w-V(r)]r^2\tilde{f}_0(r)^2\,dr, \tag{65}$$

while from (18b) and (20b) we obtain

$$V=[2mc^2/(2mc^2+w-\overline{V})]V_0$$

$$\simeq V_0-[(w-\overline{V})/2mc^2]V_0, \tag{66}$$

$$U\simeq U_0-[(w-\overline{V})/2mc^2]U_0. \tag{67}$$

Then, up to the order $1/c^2$

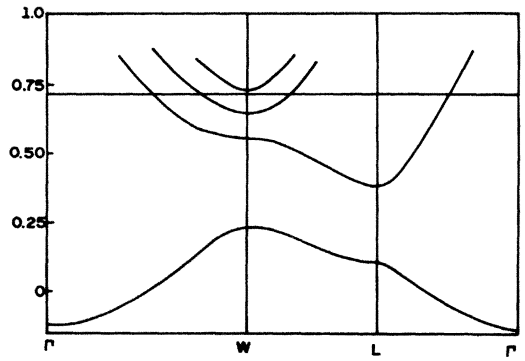

FIG. 2. Band structure of lead according to Loucks (Relativistic augmented plane wave).

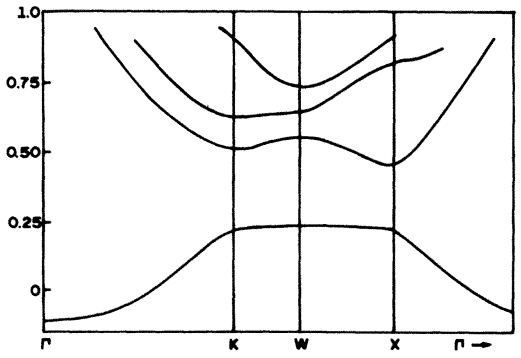

FIG. 4. Band structure of lead according to Loucks (Relativistic augmented plane wave).

$$t^{-1}=\frac{v}{u}\frac{F-V}{F-U}=\frac{v_0}{u_0}\frac{F_0-V_0}{F_0-U_0}+\frac{v_0}{u_0}\frac{V_0-U_0}{(F_0-U_0)^2}\left(\frac{w-\overline{V}}{2mc^2}F_0-\frac{1}{\hbar cR^2\tilde{f}_0(R)^2}\int_0^R[w-V(r)]r^2\tilde{f}_0(r)^2\,dr.\right). \tag{68}$$

Using Eqs. (52) for the definition of $\tilde{f}_0$, $\tilde{v}_0$, and $\tilde{u}_0$, restoring the definition of v_0 and u_0 in terms of Y_l and j_l [see Eqs. (18a) and (20a)], using the relations

$$\kappa(\kappa+1)=L(\kappa)[L(\kappa)+1], \tag{69}$$

$$\kappa+1=-\langle\kappa,\mu\,|\vec{\sigma}\cdot\vec{1}|\,\kappa,\mu\rangle, \tag{70}$$

we arrive at

$$t_\kappa^{-1}=t_{L(\kappa)}^{-1}+\alpha_{L(\kappa)}+\langle\kappa,\mu\,|\vec{\sigma}\cdot\vec{1}|\,\kappa,\mu\rangle\beta_{L(\kappa)}, \tag{71}$$

where t_l^{-1} is given by (54) and

$$\alpha_l=\frac{1}{2mc^2R^2}\frac{Ky_l'(KR)j_l(KR)-Ky_l(KR)j_l'(KR)}{[f_l'(R)j_l(KR)-Kf_l(R)j_l'(KR)]^2}\left((w-\overline{V})R^2f_l(R)f_l'(R)-\int_0^R[w-V(r)][r^2f_l'(r)^2+l(l+1)f_l(r)^2]\,dr\right), \tag{72}$$

$$\beta_l=\frac{1}{2mc^2R^2}\frac{Ky_l'(KR)j_l(KR)-Ky_l(KR)j_l'(KR)}{[f_l'(R)j_l(KR)-Kf_l(R)j_l'(KR)]^2}\left(\int_0^R[w-V(r)][2rf_l(r)f_l'(r)+f_l(r)^2]\,dr-(w-\overline{V})Rf_l(R)^2\right). \tag{73}$$

Finally, inserting (71) into Eq. (50) we obtain the following secular equation

$$(t_l^{-1}+\alpha_l)b_{l,m}^\sigma+\beta_l\sum_{m',\sigma'}\langle l,m,\sigma\,|\vec{1}\cdot\vec{\sigma}|\,l,m',\sigma'\rangle b_{l,m'}^{\sigma'}+\sum_{l',m',\sigma'}G_{l,m;l',m'}\delta_{\sigma,\sigma'}b_{l',m'}^{\sigma'}=0. \tag{74}$$

The form of Eq. (74) is very suggestive. One sees clearly the effects of mass correction and spin-orbit interaction. When using this equation one must recall that in this order, K is still given by Eq. (19), which now reads

$$K^2=(2m/\hbar^2)(w-\overline{V})+(w-\overline{V})^2/\hbar^2c^2\,. \tag{75}$$

IV. APPLICATION TO LEAD

As an application of the method we calculated the band structure of lead. This element has a fcc lattice with a parameter of 9.259 70 a.u. The neutral atom has 82 electrons and has the following electronic configuration: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^2$. The potential was calculated by summing the atomic Coulomb potentials and charge densities in the lead lattice. Then we made spherical averages inside the spheres and space averages outside to obtain the muffin-tin Coulomb potential and charge density. The exchanged interaction was included by means of the Gaspar, Kohn, and Sham formula

$$v^{ex}=-4(4\pi\rho/105.275\,78)^{1/3}\,.$$

The starting atomic Coulomb potential and charge density was obtained by means of the relativistic self-consistent method of Desclaux, Mayers, and O'Brien.[13] For the reader's convenience, we present in Table I the product of the distance to the nucleus by the potential as a function of the distance to the nucleus. The radius of the sphere is 3.273 80 a.u. and the mean value for the potential outside the spheres is -0.78619 Ry.

In Tables II and III we present a study of convergence. The entries in Table II refer to the point K of the Brillouin zone, and those of Table III to point W. The entries in the upper line represent the secular matrix dimension. Since the secular equation was not symmetrized, dimension 2 corresponds to quantum numbers $\kappa=-1$, $\mu=\frac{1}{2}$, $\mu=-\frac{1}{2}$, dimension 4 includes also the numbers $\kappa=1$, $\mu=\pm\frac{1}{2}$; for dimension 8, aside the $\kappa=\pm1$, and the corresponding μ, we have also $\kappa=-2$ with μ varying from $-\frac{3}{2}$ to $\frac{3}{2}$, and so on. The results from these tables suggest that the lower the level, the faster the convergence. This should be expected since for higher levels there are important contributions of spherical harmonics of superior l numbers. In Table IV we list the eigenvalues for some symmetry points. To obtain these values we used functions with quantum numbers κ up to $\kappa=-4$.

In Figs. 1 and 3 we show the band structure obtained by our method, and, for comparison, the band structure obtained by Loucks[14] is reproduced in Figs. 2 and 4. A better agreement is obtained for the lower bands, the third band is very distinct from that obtained by Loucks. At

least part of such discrepancies may be explained by differences in the potential. Indeed, lower bands correspond to more localized states and the potential for these electrons cannot be much different from the atomic potential. The higher levels are more sensitive to crystalline potential. Aside this fact, we do not know if Loucks made any study of convergence of his values.

V. SUMMARY

The method here developed coincides with the relativistic multiple-scattering method presented in the Refs. 1–8. Our derivation begins from the form of the four-component wave function, while in the standard derivation the wave function is always omitted. Another advantage of the present method is avoiding the guess work behind the writing of the Green's function, a task far from trivial.

Our experience with lead shows clearly that the method is very usable. As a matter of fact, in the form of Eq. (50), the secular equation differs little from that of the nonrelativistic multiple-scattering method.

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*Work supported by the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) and the Financiadora de Estudos e Projetos (FINEP).

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