PHYSICAL REVIEW B VOLUME 14, NUMBER 2 15 JULY 1976

Non-muffin-tin version of the multiple scattering method for crystals and molecules

L. G. Ferreira, A. Agostinho, and D. Lida
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, São Paulo, Brazil
(Received 15 March 1976)

We present a variational version of the multiple scattering method for non-muffin-tin potentials. Compared with a perturbational procedure where the non-muffin-tin parts of the potential are treated in the first order, the present method is both faster and more precise. In a trial numerical calculation for iron, we exhibit the virtues and main difficulties of the method.

I. INTRODUCTION

The extension of the multiple scattering method to non-muffin-tin potentials has been tried by different authors. First, we mention the work of Williams[1] and Williams and Morgan[2] which deals with general potentials, but which is too complicated to be of practical numerical interest. Aside from this general method, there are works which handle the non-muffin-tin potentials in an approximate way. In this latter category we mention the work of Keller[3] which introduced extra spheres so as to minimize the space where the muffin-tin potential is constant. These extra spheres introduce extra degrees of freedom, thus increasing the size of the secular matrix. Also in the category of approximate methods are the works of Danese and Connolly[4] and Andersen and Kasowski[5] which deal with the non-muffin-tin potentials by perturbation theory, and the work by Herman, Williams, and Johnson[6] which introduces the overlapping atomic spheres to try to account for the effects of a non-muffin-tin potential.

The muffin-tin potential is a good approximation as long as the structure is compact so that the volume where the potential is constant is relatively small. In this sense, the method proposed by John, Lehmann, and Ziesche,[7] while dealing with nonspherical potentials inside the spheres, does not solve the main problem because still requires a constant potential outside the spheres. The method developed below abandons the constant potential outside the spheres but still requires spherically symmetric potentials inside. Though the method is not exact, it is more precise, simpler, and faster than first-order perturbation theory.

II. DERIVATION OF METHOD

In order to derive the secular equation for the multiple scattering method, we consider the simplest case of a crystal with one atom per cell. The space is divided into two regions: region I is made out of the spheres with radius R circumscribing the atoms, where the potential is spherically symmetric; region II is the space outside the spheres, where the potential may vary. In region I we define the trial function as a linear combination of solutions of Schrödinger's equation for energy ϵ_0

$$\psi_{\mathrm{I}} = \sum_{\lambda} i^l C_\lambda u_l(r, \epsilon_0)\, Y_\lambda(\hat{r})\,. \tag{1}$$

In (1), λ means the pair (l, m) of angular momentum eigenvalues, $Y_\lambda(\hat{r})$ is a real spherical harmonic, $u_l(r, \epsilon_0)$ is a solution of the radial Schrödinger equation, and C_λ are the coefficients of the linear combination. The coefficients C_λ of the central atom are related to those of the atom at the cell $\vec{n}$ by the Bloch condition

$$C_\lambda(\vec{n}) = e^{i\vec{k}\cdot\vec{n}} C_\lambda\,, \tag{2}$$

where $\vec{k}$ is a wave vector in the Brillouin zone.

In region II, the trial function is a linear combination

$$\psi_{\mathrm{II}} = \sum_{\lambda} A_\lambda \psi_\lambda \tag{3}$$

of multiple scattered waves

$$\psi_\lambda = \sum_{\vec{n}} i^l e^{i\vec{k}\cdot\vec{n}} Y_\lambda(\vec{r} - \vec{n})\, n_l(K|\vec{r} - \vec{n}|)\,. \tag{4}$$

The multiple scattered wave (4) is a coherent sum of waves with angular momentum λ scattered by all the atoms of the crystal. The coefficients of this sum are chosen so that the Bloch condition is obeyed. This wave solves the Helmholtz equation

$$-\nabla^2\psi_\lambda = K^2\psi_\lambda\,, \tag{5}$$

with eigenvalue K^2. Thus the trial function has the following set of variational parameters. The coefficients C_λ of the linear combination (1) in region I, the coefficients A_λ of the linear combination (3) in region II, the energy ϵ_0 defining the radial functions in I, and K, the wave number defining the scattered waves in II. It will be seen shortly that the variational solution has

$$\epsilon_0 = \epsilon\,, \tag{6}$$

where ϵ is the energy eigenvalue of the quantum-mechanical problem, but K^2 is *not* related to this eigenvalue by

$$\epsilon = K^2 + V_{\mathrm{II}} \,. \qquad (7)$$

Only in the special case of a constant potential in the region II Eq. (7) holds. For a varying potential, this equation has no meaning, and K must be determined variationally.

Before proceeding with the variational calculus, we should also mention that the multiple scattered wave (4) assumes the form

$$\psi_\lambda = i^l Y_\lambda(\vec{\mathbf{r}}) n_l(Kr) + \sum_{\lambda'} G_{\lambda'\lambda} i^{l'} j_{l'}(Kr) Y_{\lambda'}(\vec{\mathbf{r}}) \qquad (8)$$

in the neighborhood of the sphere of the central atom. This result is central to any derivation of the multiple scattering method and has been often reviewed in the literature. The structure constants $G_{\lambda'\lambda}$ may be written in terms of the Gaunt integrals $I_\Lambda(\lambda', \lambda)$ [where $\Lambda \equiv (L, M)$, $\lambda' \equiv (l', m')$, $\lambda \equiv (l, m)$]

$$G_{\lambda'\lambda} = 4\pi \sum_\Lambda I_\Lambda(\lambda'\lambda) \Gamma_\Lambda(\vec{\mathrm{k}}, K) \,, \qquad (9)$$

where

$$\Gamma_\Lambda(\vec{\mathrm{k}}, K) = \frac{\cot(KR)}{(4\pi)^{1/2}} \delta_{\Lambda,0} - \frac{4\pi}{\Omega K j_L(KR)} \sum_{\vec{\mathrm{g}}} \left[\exp\left(- \frac{(|\vec{\mathrm{k}} + \vec{\mathrm{g}}|^2 - K^2)}{4G^2} \right) \Big/ (|\vec{\mathrm{k}} + \vec{\mathrm{g}}|^2 - K^2) \right] j_L(|\vec{\mathrm{k}} + \vec{\mathrm{g}}|R) Y_\Lambda(\vec{\mathrm{k}} + \vec{\mathrm{g}}) \,. \qquad (10)$$

In (10) the sum in $\vec{\mathrm{g}}$ extends over the reciprocal lattice. The exponential factor in the second term guarantees the absolute convergence of the series and one should take the limit of $4G^2 \to \infty$. In calculating $\Gamma_\Lambda(\vec{\mathrm{k}}, K)$ we can also use a Ewald correction term, as explained in the paper by Ham and Segal.[8] It is also worth mentioning that the multiple scattered wave of Eq. (4) can also be written as a series in the reciprocal lattice[8]

$$\psi_\lambda = - \frac{4\pi}{K\Omega j_l(KR)} \sum_{\vec{\mathrm{g}}} j_l(|\vec{\mathrm{k}} + \vec{\mathrm{g}}|R) Y_\lambda(\vec{\mathrm{k}} + \vec{\mathrm{g}}) \frac{e^{i(\vec{\mathrm{k}} + \vec{\mathrm{g}}) \cdot \vec{\mathbf{r}}}}{(\vec{\mathrm{k}} + \vec{\mathrm{g}})^2 - K^2} \exp\left(\frac{K^2 - (\vec{\mathrm{k}} + \vec{\mathrm{g}})^2}{4G^2} \right) . \qquad (11)$$

Having defined the trial function in regions I and II we must use a variational procedure to determine the energy eigenvalue and the variational parameters. In the standard version of the multiple scattering method one either forces the continuity of the trial function and its normal derivative across the sphere surfaces or uses the variational expression due to Kohn and Rostoker.[9] Both procedures are inadequate in the present case because the trial function is not an exact solution of Schrödinger's equation in region II. Thus we recur to the variational expression extensively used by us in connection with the augmented plane wave (APW) method[10,11]

$$\int_{\mathrm{II}} \psi_{\mathrm{II}}^* (H - \epsilon) \psi_{\mathrm{II}} \, dv + \int_{\mathrm{I}} \psi_{\mathrm{I}}^* (H - \epsilon) \psi_{\mathrm{I}} \, dv + \int dS \, (\partial_n \psi_{\mathrm{I}} - \partial_n \psi_{\mathrm{II}}) \psi_{\mathrm{II}}^* + \int dS \, (\psi_{\mathrm{II}} - \psi_{\mathrm{I}}) \partial_n \psi_{\mathrm{I}}^*$$
$$+ \sum_\lambda \mu_\lambda \int dS \, (\partial_n \psi_{\mathrm{II}}^* - \partial_n \psi_{\mathrm{I}}^*) Y_\lambda(\vec{\mathbf{r}}) \int dS (\partial_n \psi_{\mathrm{II}} - \partial_n \psi_{\mathrm{I}}) Y_\lambda(\vec{\mathbf{r}})^* = 0 \,. \qquad (12)$$

In this equation, H is the Hamiltonian, ∂_n means the outwards normal derivative at the sphere surfaces, and μ_λ are arbitrary real numbers. The surface integrals extend over the sphere of the central cell. As it has been explained elsewhere,[11] upon arbitrary and independent variations in the trial functions ψ_{I} and ψ_{II}, in the two regions, the energy ϵ is invariant if ψ_{I} and ψ_{II} solve the Schrödinger's equation and if they match at the sphere surface. This result holds for any value of the parameters μ_λ. Thus, these parameters may be chosen to simplify the resulting secular equation. In our case, since the trial function is not an exact solution to the Schrödinger's equation in region II, the approximate eigenvalue ϵ will depend on μ_λ to some extent.

Thus using the variational expression (12) where the trial functions are defined by (1) and (3) in terms of the variational parameters A_λ, C_λ, K, and ϵ_0, and equating to zero the variation of (12) due to an arbitrary variation of C_λ, for fixed A_λ, K, and ϵ_0, we obtain

$$(\epsilon_0 - \epsilon) C_\lambda \int_0^R r^2 u_l(r, \epsilon_0)^2 \, dr + u_l'(R, \epsilon_0) i^{-l} \int dS \, Y_\lambda(\hat{r})^* (\psi_{\mathrm{II}} - \psi_{\mathrm{I}} - R^2 \mu_\lambda \partial_n \psi_{\mathrm{II}} + R^2 \mu_\lambda \partial_n \psi_{\mathrm{I}}) = 0 \,,$$

which is satisfied if Eq. (6) holds and if

$$C_\lambda[u_l(R,\epsilon_0)-\mu_\lambda R^2u_l'(R,\epsilon_0)]=A_\lambda[n_l(KR)-\mu_\lambda R^2Kn_l'(KR)]+[j_l(KR)-\mu_\lambda R^2Kj_l'(KR)]\sum_{\lambda'}G_{\lambda\lambda'}A_{\lambda'}\,. \tag{13}$$

Equation (13) simplifies considerably if we choose

$$\mu_\lambda=j_l(KR)/R^2Kj_l'(KR)\,. \tag{14}$$

In this case, the relation between the coefficients A_λ and C_λ becomes the standard

$$A_\lambda/C_\lambda=KR^2[j_l(KR)u_l'(R,\epsilon_0)-Kj_l'(KR)u_l(R,\epsilon_0)]\,. \tag{15}$$

If we were to choose the parameters μ_λ differently from Eq. (14), the relation (13) between the trial functions in the regions I and II would be much more complicated. In that case a finite set of angular momenta inside the spheres would generate through the λ' sum in Eq. (13) an infinite series of angular momenta in the region II. Probably, in that event the method would become useless.

We also notice that (14) establishes a value for μ_λ which depends on the energy eigenvalue through K. In other words, the variational expression (12) assumes different forms for different eigenvalues. Thus approximate eigenfunctions corresponding to different levels may not be expected exactly orthogonal.

Now we turn our attention to the variations of A_λ. Instead of performing this variation fixing C_λ, ϵ_0, and K, we already use the results given by Eqs. (6), (14), and (15). Thus, upon a variation of A_λ, C_λ also varies. Equating the total variation to zero we obtain

$$\sum_{\lambda'}\left(K\int_{\mathrm{II}}\psi_\lambda^*(H-\epsilon)\psi_{\lambda'}\,dv+\frac{N_l}{J_l}\delta_{\lambda,\lambda'}+G_{\lambda\lambda'}\right)A_{\lambda'}=0\,, \tag{16}$$

where

$$N_l=n_l(KR)u_l'(R,\epsilon_0)-Kn_l'(KR)u_l(R,\epsilon_0)\,, \tag{17a}$$

$$J_l=j_l(KR)u_l'(R,\epsilon_0)-Kj_l'(KR)u_l(R,\epsilon_0)\,. \tag{17b}$$

Equation (16) is similar to the standard secular equation of the multiple scattering method. The only novelty in (16) is the appearance of a volume integral in the region II. In the Appendix we discuss the appearance of this volume integral and show that it is to be expected from first-order perturbation theory.

Finally we turn our attention to the variation of K. As it has been said earlier, for a varying potential in region II, Eq. (7) is meaningless and K must be determined variationally. When doing so, we must remember that, according to Eq. (14), the variational expression (12) is itself K dependent through μ_λ. But μ_λ is not a variational parameter in the sense that the variation of ϵ is not second order in the variation of μ_λ. Thus when varying K we must be cautious enough to vary only ψ_{II} in (12) and not μ_λ. Letting D be the symbol $D\equiv d/dK$ for fixed $A_\lambda, C_\lambda, \epsilon_0, \mu_\lambda$, from (12) we obtain

$$D\int_{\mathrm{II}}\psi_{\mathrm{II}}^*(H-\epsilon)\psi_{\mathrm{II}}\,dv+\frac{1}{R^2}\sum_\lambda\Bigg(\int dS(\partial_n\psi_{\mathrm{I}}-\partial_n\psi_{\mathrm{II}})Y_\lambda(\vec{\mathrm{r}})^*\int dS\,(D\psi_{\mathrm{II}}^*-\mu_\lambda R^2\partial_nD\psi_{\mathrm{II}}^*)Y_\lambda(\vec{\mathrm{r}})$$
$$+\int dS\,D\psi_{\mathrm{II}}Y_\lambda(\vec{\mathrm{r}})^*\int dS\,\partial_n\psi_{\mathrm{I}}^*Y_\lambda(\vec{\mathrm{r}})-\int dS\,\partial_nD\psi_{\mathrm{II}}Y_\lambda(\vec{\mathrm{r}})^*\int dS\,\psi_{\mathrm{I}}^*Y_\lambda(\vec{\mathrm{r}})\Bigg)=0\,. \tag{18}$$

Then, after a simple but lengthy calculation of the integrals in Eq. (18) we obtain

$$\sum_{\lambda\lambda'}A_\lambda^*A_{\lambda'}\Bigg(K(K^2-\epsilon)\frac{d}{dK}\int_{\mathrm{II}}\psi_\lambda^*\psi_{\lambda'}\,dv+K\frac{d}{dK}\int_{\mathrm{II}}\psi_\lambda^*v(\vec{\mathrm{r}})\psi_{\lambda'}\,dv+\frac{1}{J_l}\frac{d}{dK}(KJ_l)W_{\lambda\lambda'}$$
$$+W_{\lambda\lambda'}\frac{1}{J_{l'}}\frac{d}{dK}(KJ_{l'})-2R^2K^3\sum_{\lambda''}W_{\lambda\lambda''}Z(l'')W_{\lambda''\lambda'}\Bigg)=0\,, \tag{19}$$

where J_l has been defined in Eq. (17b),

$$Z(l)=RKj_l'(KR)^2+j_l(KR)j_l'(KR)$$
$$+[RK-l(l+1)/KR]j_l(KR)^2 \tag{20}$$

and

$$W_{\lambda\lambda'}=\int_{\mathrm{II}}\psi_\lambda^*[K^2-\epsilon+v(\vec{\mathrm{r}})]\psi_{\lambda'}\,dv\,. \tag{21}$$

In the special case of a constant potential in region II

$$v(\vec{\mathrm{r}})=V_{\mathrm{II}}\,,$$

the obvious solution of Eq. (19) is

$$K^2=\epsilon-V_{\mathrm{II}}\,.$$

Then Eq. (16) reduces to the standard multiple scattering secular equation. In the general case

TABLE I. Potential in the region II.

(a)	Radius of touching spheres	2.436 68 a.u.
(b)	Potential outside the touching spheres	−1.569 57 Ry
(c)	Potential at the surface of touching spheres	−1.674 18 Ry
(d)	Radius of the reduced spheres	1.722 99 a.u.
(e)	Potential at the surface of the reduced spheres	−2.488 58 Ry
(f)	Potential in the region between touching and reduced spheres	$r \times v(r)$ linear with r
(g)	Average value of the potential outside the reduced spheres (region II)	−1.841 63 Ry

of a varying potential in region II, one would find the eigenvalues ϵ according to Eq. (16), in a coarse net of K values. For each pair (ϵ, K) found, one would calculate the average value of the left-hand side of Eq. (19). By a simple interpolation for a null average value, one would determine the approximate energy eigenvalue. As long as the volume integrals, appearing in Eqs. (16) and (19), can be well done, the method is remarkably simple because the finding of the solution of Eq. (16), for a given K, is simplified since ϵ appears only multiplying the volume integral and in the diagonal term N_l/J_l. Thus, the usefulness of the present method depends primarily on our ability to perform the volume integrals in region II, occurring in Eqs. (16) and (19).

We also mention that ϵ is not expected to be much dependent on the value of K because the volume integral in (16) works as a first-order correction to the deviations of K (see Appendix). As long as K is chosen in such a way that Eq. (7) is approximately obeyed for a representative value V_{II} of the potential in the region II, the resulting value of ϵ should be approximately correct. In our trial calculations we observed that, near the optimal value of K given by (19), the sensitivity of ϵ with K^2, that is the derivative $|d\epsilon/d(K^2)|$, was of the order of 1%. Thus, one is allowed to neglect Eq. (19), in favor of an auxiliary condition such as Eq. (7), where V_{II} is interpreted as a representative value of the potential in region II.

III. NUMERICAL CALCULATION

In order to gain insight into the power and difficulties of the method, we made a test calculation for a model potential for face-centered-cubic iron. Initially the spheres were made to touch and the potential was trimmed to be spherically symmetric inside the spheres and constant in the region outside. For this muffin-tin potential, the method is exact and coincides with the standard Korringa-Kohn-Rostoher (KKR) method. In this situation, using waves with angular momentum $l=2$, we calculated the d levels at Γ (center of the Brillouin zone) and found the eigenvalues $\epsilon = -0.983$ Ry (for the triply degenerate level) and $\epsilon = -0.885$ Ry (for the doubly degenerate level). Then, maintaining the potential but reducing the radius of the spheres by a factor $\sqrt{2}$, we recalculated the energy levels according to Eq. (16). With respect to the reduced spheres, the potential is no longer constant in the region II because it varies in the space between the new and old spheres. In Table I we show the data concerning the potential in the region II and its spatial variation.

After verifying that $d\epsilon/d(K^2)$ was very small in the vicinity of ϵ and K which satisfy Eqs. (16) and (19), we abandoned Eq. (19) altogether, in favor of the simpler Eq. (7) with V_{II} defined as the following average:

$$V_{\text{II}} = \sum_{\lambda\lambda'} A_\lambda^* A_{\lambda'} \int_{\text{II}} \psi_\lambda^* v(\vec{r}) \psi_{\lambda'}\, dv \Big/ \sum_{\lambda\lambda'} A_\lambda^* A_{\lambda'} \int_{\text{II}} \psi_\lambda^* \psi_{\lambda'}\, dv\,. \tag{22}$$

Though this substitution simplified considerably the numerical problem, the volume integrals occurring in (16) and (22) turned out to be the bottleneck of the method. These integrals were calculated using Eq. (11) as the representation for the scattered waves. Thus

$$\int_{\text{II}} \psi_\lambda^* v(\vec{r}) \psi_{\lambda'} dv = \frac{16\pi^2}{K^2 \Omega^2 j_l(KR) j_{l'}(KR)} \sum_{\vec{g}} \sum_{\vec{g}'} j_l(|\vec{k}+\vec{g}|R) j_{l'}(|\vec{k}+\vec{g}'|R) Y_\lambda(\vec{k}+\vec{g}) Y_{\lambda'}(\vec{k}+\vec{g}')$$

$$\times \{[(\vec{k}+\vec{g})^2 - K^2][(\vec{k}+\vec{g}') - K^2]\}^{-1} \int_{\text{II}} v(\vec{r}) \exp[i(\vec{g}' - \vec{g})\cdot\vec{r}]\, dv\,, \tag{23}$$

TABLE II. Calculated eigenvalues as functions of the number of reciprocal-lattice vectors in the double sums.

Number of vectors	Eigenvalues (Ry)	Comments
1	−0.953 and −0.855	Equivalent to muffin-tin potential whose constant equals the average potential in region II
15	−0.959 and −0.866	
59	−0.972 and −0.873	
113	−0.977 and −0.877	
Exact	−0.983 and −0.885	Results calculated with the large spheres (see text)

where we drop the exponential factors of Ewald's method since, as it stands, the double sum in Eq. (23) is absolutely convergent.

The double sum in Eq. (23) is slowly convergent as it can be readily concluded from the results in Table II. In this table we present the energy eigenvalues as functions of the number of reciprocal lattice vectors used in the double sums of Eq. (23). The result for just one vector, $\vec{g}=(000)$, is exactly equivalent to a muffin-tin potential whose constant is the average potential in the region II. This can be seen from (22), which reduces to the ratio

$$\int_{\text{II}} v(\vec{r})\,dv \bigg/ \int_{\text{II}} dv$$

in the case when just one $\vec{g}$ is taken in the double sum. Table II shows that the energy eigenvalues tend to the exact values as the double sum is made with more precision, although the convergence is not as fast as one would like.

IV. CONCLUSIONS

The method presented above, and embodied by Eqs. (16) and (19), or (16), (7), and (22), is the simplest generalization of the multiple scattering method for non-muffin-tin potentials that has been presented so far. It is not an exact method, in the sense that the trial function is not a solution to Schrödinger's equation in region II. Nevertheless, it is a variational method and yields results that are more accurate than a first-order perturbation theory. Its weak point lies in the calculation of the volume integrals of Eqs. (19) or (22). In the multiple scattering method, a volume integral such as

$$\int_{\text{II}} \psi_\lambda^* \psi_{\lambda'}\,dv$$

can be transformed into a surface integral which can be readily calculated, but that is not the case of

$$\int_{\text{II}} \psi_\lambda^* v(\vec{r}) \psi_{\lambda'}\,dv\ .$$

On the other hand, the calculation of this integral is unavoidable even if we decide to deal with non-muffin-tin potentials by first-order perturbation theory. When we are faced with the calculation of such integrals in crystals we begin to wonder why use the multiple scattering method and not a simple APW method. Indeed, the APW method handles non-muffin-tin potentials in a very handsome way. In the calculation of the volume integrals, the speed of the multiple scattering method is lost. Thus, for crystals with non-muffin-tin potentials, the multiple scattering method seems to lose its many assets compared with other methods. On the other hand, for molecules, the multiple scattering method still stands as the only choice. In this case, we think that the best way to study the effects of a non-muffin-tin potential is through the present formalism.

APPENDIX

Let us consider the standard muffin-tin multiple scattering method. In this case,

$$K^2 = \epsilon - V_{\text{II}}$$

holds, V_{II} is the constant potential in region II, and from Eq. (16) we exclude the volume integral. Thus the secular equation becomes

$$\det[(N_l/J_l)(K^2,\epsilon)\delta_{\lambda\lambda'} + G_{\lambda\lambda'}(K^2)] = 0\ , \tag{A1}$$

where we explicitly state that the ratio N_l/J_l depends on ϵ through the radial function $u_l(R,\epsilon)$ and through K^2 occurring in the arguments of the Bessel functions.

Consider now a variation δV_{II} in the constant potential V_{II}. If Eq. (A1) is to hold, the eigenvalue must change by $\delta\epsilon$. Then

$$\sum_{\lambda\lambda'} M_{\lambda\lambda'}\left\{\left[\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\delta\epsilon-\left[\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\delta V_{\text{II}}\right\}=0\,.$$

$M_{\lambda\lambda'}$ is the minor in the determinant of Eq. (A1) corresponding to the element (λ,λ'). It is well known that this minor is proportional to the product $A^*_\lambda A_{\lambda'}$ of the normalized coefficients defining the eigenfunction (3). Thus

$$\frac{\delta\epsilon}{\delta V_{\text{II}}}=\left\{\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\left[\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\right\}\Big/\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\left[\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\,. \tag{A2}$$

The ratio $\delta\epsilon/\delta V_{\text{II}}$ is just the probability P_{II} of finding the particle in the region II. Then the probability of finding it in region I is

$$P_{\text{I}}=1-P_{\text{II}}$$

or

$$P_{\text{I}}=\left[\sum_{\lambda} A^*_\lambda A_\lambda\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)\right]\Big/\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\left[\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\,. \tag{A3}$$

For future reference, and from Eq. (17) we obtain

$$\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)=-\frac{1}{KR^4J^2_l}\int_0^R r^2u(r,\epsilon)^2\,dr\,. \tag{A4}$$

The probability P_{I} can be also calculated from (1). Thus

$$P_{\text{I}}=\sum_{\lambda} C^*_\lambda C_\lambda\int_0^R r^2u_l(r,\epsilon)^2\,dr\,.$$

But from (15) we obtain

$$P_{\text{I}}=\sum_{\lambda} A^*_\lambda A_\lambda\frac{1}{K^2R^4J^2_l}\int_0^R r^2u_l(r,\epsilon)^2\,dr\,, \tag{A5}$$

and comparing (A5) with (A3) we see that the normalized coefficients A_λ satisfy

$$\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\left[\frac{\partial}{\partial\epsilon}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]=-K\,. \tag{A6}$$

When using Eq. (A6) one must remember that it is valid only when the potential is muffin tin.

Then, using (A6) in (A2), we obtain

$$P_{\text{II}}=\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\int_{\text{II}}\psi^*_\lambda\psi_{\lambda'}\,dv=-\frac{1}{K}\sum_{\lambda\lambda'} A^*_\lambda A_{\lambda'}\left[\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]$$

for the probability of the particle being found in region II.

Finally suppose we choose a K^2 not exactly equal to $\epsilon-V_{\text{II}}$. Within the linear approximation, (A1) may be written

$$\begin{aligned}
0&=\det[(N_l/J_l)(\epsilon-V_{\text{II}},\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(\epsilon-V_{\text{II}})]=\det[(N_l/J_l)(K^2+(\epsilon-V_{\text{II}}-K^2),\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(K^2+(\epsilon-V_{\text{II}}-K^2))]\\
&=\det\left\{\frac{N_l}{J_l}(K^2,\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(K^2)+(\epsilon-V_{\text{II}}-K^2)\left[\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{dG_{\lambda\lambda'}}{dK^2}\right]\right\}\\
&=\det\left(\frac{N_l}{J_l}(K^2,\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(K^2)\right)+(\epsilon-V_{\text{II}}-K^2)\sum_{\lambda\lambda'} M_{\lambda\lambda'}\left[\frac{\partial}{\partial K^2}\left(\frac{N_l}{J_l}\right)\delta_{\lambda\lambda'}+\frac{d}{dK^2}G_{\lambda\lambda'}\right]\\
&=\det\left(\frac{N_l}{J_l}(K^2,\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(K^2)\right)+K(V_{\text{II}}+K^2-\epsilon)\sum_{\lambda\lambda'} M_{\lambda\lambda'}\int_{\text{II}}\psi^*_\lambda\psi_{\lambda'}\,dv\\
&=\det\left(K(V_{\text{II}}+K^2-\epsilon)\int_{\text{II}}\psi^*_\lambda\psi_{\lambda'}\,dv+\frac{N_l}{J_l}(K^2,\epsilon)\delta_{\lambda\lambda'}+G_{\lambda\lambda'}(K^2)\right)=0\,.
\end{aligned}$$

The last equality is a reproduction of Eq. (16) for muffin-tin potentials. Thus we see that Eq. (16), for muffin-tin potentials, is at least as good as first-order perturbation. Being a variational result, Eq. (16) should go beyond first-order perturbation theory, and this result should be still valid for more general potentials.

---

[1] A. R. Williams, Int. J. Quantum Chem. 85, 89 (1974).

[2] A. R. Williams and J. van W. Morgan, J. Phys. C 7, 37 (1974).

[3] J. Keller, J. Phys. C 4, 3143 (1971).

[4] J. B. Danese and J. W. D. Connolly, Int. J. Quantum Chem. 75, 279 (1973).

[5] O. K. Andersen and R. V. Kasowski, Phys. Rev. B 4, 1064 (1971).

[6] F. Herman, A. R. Williams, and K. H. Johnson, J. Chem. Phys. 61, 3508 (1974).

[7] W. John, G. Lehmann, and P. Ziesche, Phys. Status Solidi B 53, 287 (1972).

[8] F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).

[9] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[10] L. G. Ferreira, J. R. Pereira, D. Lida, and A. Agostinho, J. Phys. C 7, 1076 (1974).

[11] L. G. Ferreira, M. J. Oliveira, E. Z. Silva, G. G. Graça, and B. J. O. Franco, J. Phys. C 8, 992 (1975).