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New Version of the Modified Augmented-Plane-Wave Method*

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A method is presented to calculate electronic band structures for a general one-electron potential. Both the wave functions and their gradients are continuous everywhere in the crystal. As a test, calculations for paramagnetic Ni, Cu, and Al by Hanus, Burdick, and Segall, respectively, were repeated, using their muffin-tin potentials.

I. INTRODUCTION

Among the different methods to calculate the band structure of solids, the augmented-plane-wave (APW) method proposed by Slater[1,2] has proved particularly useful. It is based on the fact that the crystal potentials near an atomic site are approximately spherically symmetric. Therefore, the crystal will be divided into several parts by constructing a sphere (radius r_i) about each atomic site. The wave function is expanded inside each sphere in terms of radial functions multiplied by spherical harmonics; in the region between the spheres the wave function is expanded in a Fourier series of plane waves. Across the surfaces of the spheres, the APW method in its original form makes the partial waves continuous, however, for the lower values of the azimuthal quantum number l only. Usually all the calculations using the APW method are based on a muffin-tin potential, which is spherically symmetric inside the atomic spheres and has a constant value outside.

Within the one-electron approximation, several improvements of the APW method are desirable: (i) exact continuity of both the wave functions and their first derivatives on the surfaces of the APW spheres (this is a necessary requirement if the wave functions are to be used to calculate matrix elements, in particular, those of the momentum operator and functions thereof), (ii) generalization of the method to allow for non-muffin-tin potentials (this step should be done if the band structure is calculated in a self-consistent manner), (iii) orthogonality of the wave functions of the valence electrons to the wave functions of the core electrons. Preferably the core electrons should be described by Bloch functions also.

In addition, one would like to have a formalism which can be handled on a computer using standard techniques of numerical analysis.

Different modifications of the APW method[3-10] have been proposed with the above-mentioned goals. The version previously proposed by one of the present authors[5,8,9] incorporates the first requirement. Further, it allows for a nonconstant potential in the plane-wave region as do the formulations of Leigh,[3] Schlosser and Marcus,[4] and De Cicco.[6] General potentials have been studied by Marcus[7] and others.[8-10] In the 1937 formulation of the APW method, the wave functions of the valence electrons are orthogonal to those of the core states if the latter are also determined by the APW method. The aim of this paper is to describe a new version of the modified-augmented-plane-wave method (MAPW) which produces wave functions of the valence electrons orthogonal to the wave functions of the core electrons and which is especially suited for computers. Applications to paramagnetic Ni, Cu, and Al are reported with the special view towards comparing the results with earlier calculations.[11-13]

II. DESCRIPTION AND DISCUSSION OF METHOD

A. MAPW Trial Functions

As in the original APW method, we approximately solve the one-electron Schrödinger equation by the

equivalent variational principle. In contrast to other versions, however, we do not work with exact solutions of the Schrödinger equation inside the APW sphere, even if the potential is spherically symmetric in this region. As a trial function for the Rayleigh-Ritz procedure we rather use

$$\psi_{\vec{k}}^{I}(\vec{r}) = \sum_{n} \sum_{l=0;m}^{L} (2l+1) i^{l+2m} A_{nlm} R_{nl}(r) Y_{lm}(\vec{r}^{\,0}) + \sum_{\vec{k}_j} \sum_{l=L+1;m}^{\infty} v(\vec{k}_j)(2l+1) i^{l+2m} Y_{l,-m}(\vec{k}_j^{\,0}) j_l(k_j r) Y_{lm}(\vec{r}^{\,0}) \tag{1a}$$

$$= \sum_{\vec{k}_j} v(\vec{k}_j) e^{i\vec{k}_j\vec{r}} + \sum_{l=0;m}^{L} (2l+1) i^{l+2m} \left(\sum_{n} A_{nlm} R_{nl}(r) - \sum_{\vec{k}_j} v(\vec{k}_j) j_l(k_j r) Y_{l,-m}(\vec{k}_j^{\,0}) \right) Y_{lm}(\vec{r}^{\,0}) \quad \text{for } r < r_i \ , \tag{1b}$$

$$\psi_{\vec{k}}^{II}(\vec{r}) = \sum_{\vec{k}_j} v(\vec{k}_j) e^{i\vec{k}_j\vec{r}} \qquad \text{for } r > r_i \ . \tag{2}$$

Here $\vec{r}^{\,0}$ and $\vec{k}_j^{\,0}$ are unit vectors. The electron states are characterized by the reduced wave vector $\vec{k}$. We defined $\vec{k}_j = \vec{k} + \vec{K}_j$, where $\vec{K}_j$ denotes a reciprocal-lattice vector. The expansion coefficients A and v are obtained from the condition that the energy be stationary. $Y_{l,m}$ and j_l denote spherical harmonics and spherical Bessel functions, respectively. The radial dependence of the partial waves with $l \leqq L$ inside the APW sphere is described by the functions $R_{nl}(E_{nl}, r)$, which are solutions of the differential equation

$$R_{nl}'' + (2/r)R_{nl}' + [E_{nl} - l(l+1)/r^2 - V_{\text{sph}}(r)]R_{nl} = 0 \ , \tag{3}$$

where $V_{\text{sph}}(r)$ denotes the spherical mean value of the potential $V(\vec{r})$. In Slater's APW version,[14] as well as in the earlier MAPW procedure, the complete set of the R_{nl}'s was generated by the requirement that all partners have the same logarithmic derivative for $r = r_i$. This results in a severe restriction of the flexibility of the r dependence of the trial functions in the vicinity of the sphere $r = r_i$ and necessitates a further variation of the E_{nl}'s. Since this second variation turns out to be very time consuming in practice, we consider solutions of Eq. (3) in the interval $0 \leq r \leq r_0$ with $r_0 > r_i$, and orthogonalize them as before. The different R_{nl}'s for a given l having the same logarithmic derivative for $r = r_0$,

$$c_l = R_{nl}'(E_{nl}, r_0)/R_{nl}(E_{nl}, r_0) \ ,$$

are distinguished by the index n which counts the number of zeros in $0 \leq r \leq r_0$. The values of the c_l's are not determined at this stage. It has proved advantageous to fix them by choosing a value of E which has the order of magnitude of the expected energies of the valence band, and by calculating $c_l = R_l'(E, r_0)/R_l(E, r_0)$ using Eq. (3). In the cases of Ni, Cu, and Al, we found (i) that the final results are neither sensitive to the choice of the c_l's, even if a small number of R_{nl}'s is used, nor to the choice of the value of r_0 which was varied in the range from $1.2r_i$ to $2r_i$; and (ii) that this procedure yields R_{nl}'s which are well suited to describe the core states, too. The first-mentioned property allows one to take a single fixed set of c_l's for all states having the same order of magnitude of energy, with the consequence that only the coefficients A and v depend on $\vec{k}$.

Given a spherically symmetric potential for $r \leq r_i$, the APW method leads to exact solutions of the Schrödinger equation inside the sphere for the eigenvalue $E_{\vec{k}}$, which in practice, however, can only be achieved iteratively. In the present version, the partial waves for both $l \leq L$ and $l > L$ generally do not have this property, as in the APW method for a nonspherical potential in $r \leq r_i$. Despite this fact, our trial functions have the correct r dependence near the atomic site, where $|V_{\text{sph}}(r) + l(l+1)/r^2| \gg |E_{\vec{k}}|$. Furthermore, we find it more appropriate to minimize the mean error in the whole cell rather than to solve the Schrödinger equation in one region exactly.

In Eq. (1a), the second sum implies the continuity of the partial waves and their derivatives for $l > L$. In order to fulfill these conditions for $l \leq L$ also, we demand

$$\sum_{n} A_{nlm} R_{nl}(r_i) - \sum_{\vec{k}_j} v(\vec{k}_j) Y_{l,-m}(\vec{k}_j^{\,0}) j_l(k_j r_i) = 0 \ , \tag{4}$$

$$\sum_{n} A_{nlm} R_{nl}'(r_i) - \sum_{\vec{k}_j} v(\vec{k}_j) Y_{l,-m}(\vec{k}_j^{\,0}) j_l'(k_j r_i) = 0 \ . \tag{5}$$

Furthermore, the presence of the second sum in Eq. (1a) makes it possible to work with a rather small value of L. Usually it is sufficient to limit L to 2. The trial functions in the representations (1b) and (2) consist of only finite sums. This proves advantageous for the calculation of matrix elements with these functions.

B. Variational Principle

We proceed in the usual manner and make the expectation value of the energy stationary under

the constraints of normalization and continuity of the wave function and its derivative, as described by Eqs. (4) and (5). These conditions are incorporated by means of Lagrange multipliers $-E_{\vec{k}}^{*}$, α_{lm}, and β_{lm}, respectively. We get the following secular equations:

$$\sum_{j'}(H_{jj'}-E_{\vec{k}}^{*}\Omega_{jj'})v(\vec{k}_{j'})+\sum_{n}\sum_{l=0,m}^{L}H_{j,nlm}A_{nlm}-\sum_{l=0;m}^{L}Y_{l,-m}^{*}(\vec{k}_j^0)j_l(k_jr_i)\alpha_{lm}-\sum_{l=0;m}^{L}Y_{l,-m}^{*}(\vec{k}_j^0)j_l'(k_jr_i)\beta_{lm}=0 \quad \text{for all } j, \tag{6}$$

$$\sum_{j}H_{nlm,j}v(\vec{k}_j)+\sum_{n'}\sum_{l'=0;m'}^{L}(H_{nlm,n'l'm'}-E_{\vec{k}}^{*}\delta_{ll'}\delta_{mm'}\Omega_{nlm,n'l'm'})A_{n'l'm'}+R_{nl}(r_i)\alpha_{lm}+R_{nl}'(r_i)\beta_{lm}=0 \quad \text{for all } n, l, m. \tag{7}$$

The following abbreviations have been used:

$$\Omega_{jj'}=\Omega_0\delta_{jj'}-4\pi\sum_{l=0}^{L}(2l+1)P_l(\vec{k}_j^0\cdot\vec{k}_{j'}^0)\int_0^{r_i}j_l(k_jr)j_l(k_{j'}r)r^2dr, \tag{8}$$

$$\Omega_{nlm,n'l'm'}=4\pi(2l+1)[(l+m)!/(l-m)!]\int_0^{r_i}R_{nl}(r)R_{n'l}(r)r^2dr, \tag{9}$$

$$H_{jj'}=\tfrac{1}{2}(k_j^2+k_{j'}^2)\Omega_{jj'}+\Omega_0\tilde{V}(|\vec{K}_j-\vec{K}_{j'}|)+4\pi\int_0^{r_i}V_{\text{sph}}(r)\{j_0(|\vec{K}_j-\vec{K}_{j'}|r)-\sum_{l=0}^{L}(2l+1)P_l(\vec{k}_j^0\cdot\vec{k}_{j'}^0)\,j_l(k_jr)\,j_l(k_{j'}r)\}\,r^2dr$$
$$-\left(\sum_{l=0;m}^{L}\sum_{l'=0;m'}^{L}+\sum_{l=0;m}^{L}\sum_{l'=L+1;m'}^{\infty}+\sum_{l=L+1;m}^{\infty}\sum_{l'=0;m'}^{L}\right)S_{jlm,j'l'm'}, \tag{10}$$

$$H_{j,n'l'm'}=H_{n'l'm',j}^{*}=(2l'+1)i^{l'+2m'}\sum_{l=L+1;m}^{\infty}(2l+1)i^{l+2m}\,Y_{l,-m}^{*}(\vec{k}_j^0)\sum_{l''>0}^{\infty}\int Y_{lm}^{*}\,Y_{l'm'}K_{l''}\,d\omega\int_0^{r_i}j_l(k_jr)R_{n'l'}(r)\tilde{V}(l'',r)r^2\,dr, \tag{11}$$

$$H_{nlm,n'l'm'}=2\pi(2l+1)[(l+m)!/l-m)!]\delta_{ll'}\delta_{mm'}(E_{nl}+E_{n'l})\int_0^{r_i}R_{nl}(r)R_{n'l}(r)r^2\,dr$$
$$+\sum_{l''>0}^{l+l'}(2l+1)(2l'+1)i^{l'-l+2(m'-m)}\int Y_{lm}^{*}Y_{l'm'}K_{l''}\,d\omega\int_0^{r_i}R_{nl}(r)R_{n'l'}(r)\tilde{V}(l'',r)r^2\,dr, \tag{12}$$

$$S_{jlm,j'l'm'}=(2l+1)(2l'+1)i^{l'-l+2(m'-m)}Y_{l,-m}^{*}(\vec{k}_j^0)Y_{l',-m'}(\vec{k}_{j'}^0)\sum_{l''>0}^{\infty}\int Y_{lm}^{*}Y_{l'm'}K_{l''}\,d\omega\int_0^{r_i}j_l(k_jr)j_{l'}(k_{j'}r)\tilde{V}(l'',r)r^2\,dr. \tag{13}$$

Ω_0 denotes the volume of the atomic cell. The deviation of the potential from muffin-tin form, $\tilde{V}(\vec{r})$, is expressed by

$$\tilde{V}(\vec{r})=\begin{cases}V(\vec{r})-V_{\text{sph}}(r) & \text{for } r\le r_i\\ V(\vec{r}) & \text{for } r>r_i\end{cases}. \tag{14}$$

It may be expanded in a Fourier series

$$\tilde{V}(\vec{r})=\sum_{\vec{K}_j}\tilde{V}(\vec{K}_j)e^{i\vec{K}_j\vec{r}}. \tag{15}$$

Inside the APW sphere, it is appropriate to express the angular dependence by lattice harmonics[15]

$$\tilde{V}(\vec{r})=\sum_{l>0}^{\infty}\tilde{V}(l,r)K_l(\vec{r}^0). \tag{16}$$

The surface integrals extend over the unit sphere and can be evaluated using Clebsch-Gordan coefficients. In Eqs. (10) and (11), several l sums occur which extend from $L+1$ to ∞. Since the individual terms contain one of the integrals

$$\int_0^{r_i}j_l(k_jr)R_{n'l'}(r)\tilde{V}(l'',r)r^2\,dr$$

or

$$\int_0^{r_i}j_l(k_jr)j_{l'}(k_{j'}r)V(l'',r)r^2\,dr,$$

which in most cases turns out to diminish rapidly with growing values of l, convergence is ensured.[16]

C. Reduction of Eigenvalue Problem

Briefly we should like to comment on the nu-

merical solution of the eigenvalue problem, which has the form

$$\begin{pmatrix} \underline{H}_{11} & \underline{H}_{12} & & \underline{C}_1^\dagger & \underline{C}_2^\dagger \\ \underline{H}_{12}^\dagger & \underline{H}_{22} & & & \\ \underline{C}_1 & & & & \\ \underline{C}_2 & & \underline{0} & & \end{pmatrix} \begin{pmatrix} \underline{v} \\ \underline{A} \\ \underline{\alpha} \\ \underline{\beta} \end{pmatrix} = E \begin{pmatrix} \underline{\Omega}_1 & \underline{0} & & \underline{0} \\ \underline{0} & \underline{\Omega}_2 & & \\ & & & \\ & \underline{0} & & \underline{0} \end{pmatrix} \begin{pmatrix} \underline{v} \\ \underline{A} \\ \underline{\alpha} \\ \underline{\beta} \end{pmatrix}, \tag{17}$$

where the submatrices $\underline{H}_{ij}$ generate the matrix element $\langle\psi|H|\psi\rangle$, the $\underline{\Omega}_i$ guarantee the normalization of ψ, and finally, where the $\underline{C}_i$ force the wave function and its gradient to be continuous. In (17) the first two equations correspond to Eqs. (6) and (7), whereas the third and fourth equations correspond to the requirements of continuity, Eqs. (4) and (5).

Clearly, one tries to reduce the rank of the eigenvalue problem. The main object in view should be, however, to retain a linear eigenvalue problem, because nonlinear eigenvalue problems can only be solved by directly searching for the zeros of the secular determinant. In our case, it is possible to eliminate twice as many equations as the vectors of the Lagrange multipliers α_{lm} and β_{lm} have components. The elimination can be done such that the Hermitian property of both matrices involved is conserved. Since all rows of $\underline{C}_1$ and $\underline{C}_2$ are linearly independent – otherwise any energy E would solve the eigenvalue problem – we can take a sequence of Gauss elimination steps to remove the submatrices $\underline{C}_1$ and $\underline{C}_2$. These steps cannot change any element of $\underline{C}_1^\dagger$ or $\underline{C}_2^\dagger$. Therefore it is possible to perform the transposed elimination steps for $\underline{C}_1^\dagger$ and $\underline{C}_2^\dagger$. It would not be suitable to carry out the elimination analytically in our formulas since any of the denominators which arise may vanish or become very small, leading to numerical risks. As a consequence of the elimination process, all zero eigenvalues of the semipositive definite matrix on the right-hand side of Eq. (17) are removed, so that its Cholesky decomposition[17] becomes possible, and we get a Hermitian eigenvalue problem of standard form $\underline{A}\,\underline{y} = E\,\underline{y}$. For most computers, subroutines are available which simultaneously yield, with high speed and accuracy, all energy eigenvalues as well as eigenvectors in a given energy interval. If we take as a realistic example a $\vec{k}$ point without any symmetry, we have, for instance, $9\alpha_{lm}$'s, $9\beta_{lm}$'s, $18A_{nlm}$'s, and $51v_j$'s, consequently, a total rank of 87. After elimination the rank will be reduced to 51.

For highly symmetric directions of the $\vec{k}$ vector, the size of the eigenvalue problem may, of course, be further reduced by group-theoretical arguments.[18]

D. Orthogonality to Core States

The formalism developed above yields both valence states and core states which are orthogonal to one another. In the case of a low-lying core state, an essential simplification is possible since the wave function falls off very rapidly inside the APW sphere and can be regarded to be zero at its surface. As a consequence, the coefficients v and the Lagrange multipliers will turn out to be negligibly small. Furthermore, in the cases of Ni, Cu, and Al, we found that by choosing the c_l's as described in Sec. II A, only one of the coefficients A will be essentially different from zero. This core state may approximately be determined by solving the Schrödinger equation of the corresponding atomic problem with the actual crystal potential. This procedure leads to $\vec{k}$-independent wave functions which are orthogonal both to one another and to the valence functions. Noticing this property, we can omit those partners R_{nl} which represent the low-lying core states in the ansatz for the valence states.

III. RESULTS

Using the muffin-tin potentials of Hanus,[11] Burdick,[12] and Segall,[13] the band structure and the wave functions were determined for paramagnetic Ni, Cu, and Al in the $\langle 001\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions of $\vec{k}$ space, limiting ourselves to $L = 2$. In order to test the convergence, the number of partners R_{nl} was increased from 2 to 7 and the number of plane waves from 15 to more than 100. As a typical example, we show in the first three columns of Table I a $\vec{k}$ point in the middle of the Δ_1 line of the first conduction band of Cu. We remark that we achieve an accuracy better than 0.005 Ry if we restrict ourselves to $2n$ values and 51 plane waves. The same accuracy was established in all cases considered.

Comparing our results with those of Burdick and Segall, we found that the deviations of the energy values for Cu were constantly within the limits of accuracy of 0.01 Ry and less than 0.008 Ry for Al.

For Ni, the $\vec{k}$ dependence of the energies for the three directions of high symmetry, as determinated by the MAPW procedure, is plotted in Fig. 1. As compared to Hanus's results, we always find for the conduction electrons somewhat lower energy values. These deviations show a weak $\vec{k}$ dependence and are most pronounced at Γ_1 with 0.05 Ry. On the average, these deviations are about 0.02 Ry. In the view of the excellent agreement in the cases of Cu and Al, we have some confidence in the Ni results, yet we cannot understand the dis-

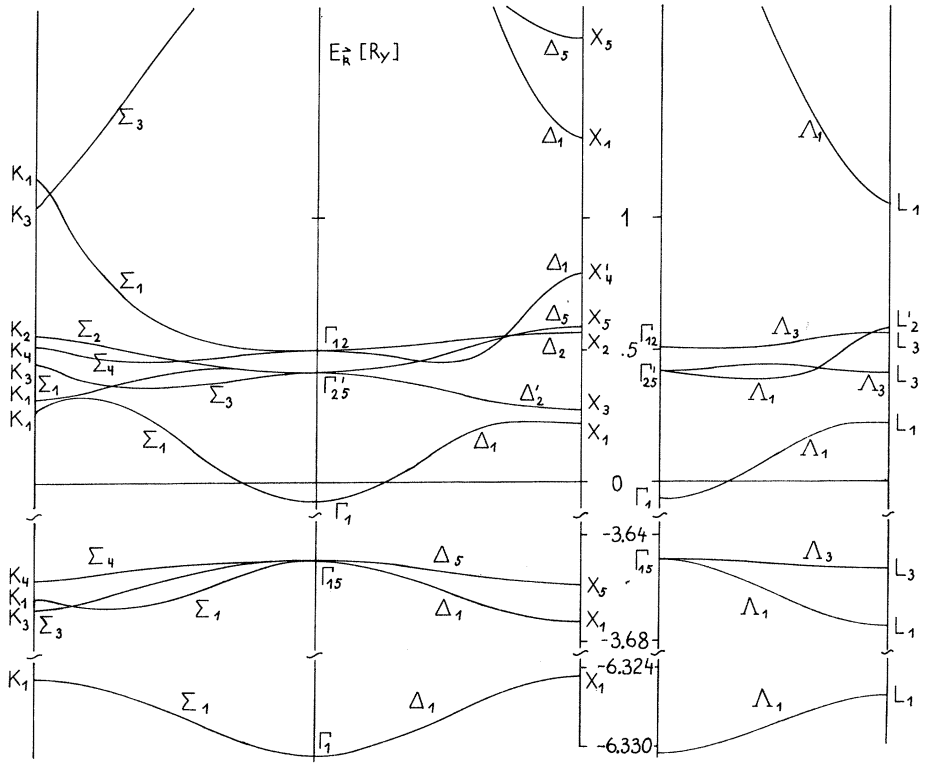

FIG. 1. $E_{\vec{k}}$ versus $\vec{k}$ along the ⟨110⟩, ⟨001⟩, and ⟨111⟩ directions in the Brillouin zone in nickel. Representation labels are in the usual Bouckaert-Smoluchowski-Wigner notation.

crepancy between our results and those of Hanus.

We also calculated the highest-lying core bands. In Table II we list the energies for $\vec{k}=0$, $E_{\vec{k}=0}$, and the bandwidths ΔE.

TABLE I. Dependence of E_k and σ^2_{III} on the number of plane waves J and the number of partners R_{nl} for a fixed l, N.

1	2	3	4
J	N	E_k (Ry)	σ^2_{III} (Ry^2)
	2	−0.797 439	0.051
	3	−0.845 422	0.021
15	4	−0.846 226	0.019
	5	−0.846 473	0.022
	6	−0.846 584	0.026
	2	−0.845 170	0.0333
	3	−0.846 997	0.0073
51	4	−0.847 188	0.0050
	5	−0.847 233	0.0055
	6	−0.847 253	0.0065
	4	−0.847 309	0.0046
	5	−0.847 371	0.0013
89	6	−0.847 376	0.0011
	7	−0.847 378	0.0012
	4	−0.847 326	0.004 30
	5	−0.847 384	0.000 64
113	6	−0.847 389	0.000 29
	7	−0.847 390	0.000 29

Since it is well known that variational principles need not yield a reasonable approximation for the true eigenvectors even if the eigenvalue is converging well, we have to look for a criterion to judge the accuracy of the wave functions.

An obvious criterion would be

$$\sigma_I = \int \psi^*_{\vec{k}}(H - E_{\vec{k}})\psi_{\vec{k}} d\tau / \int \psi^*_{\vec{k}}\psi_{\vec{k}}\, d\tau \ ,$$

since the value of this expression will vanish for the exact solution. However, it is easy to verify that this is true for any trial function, as a consequence of the demand that σ_I be stationary.

Another test for the accuracy of the wave function would be to evaluate

$$\sigma_{II}(\vec{r}) = H\psi_{\vec{k}}(\vec{r})/\psi_{\vec{k}}(\vec{r}) - E_{\vec{k}}$$

at every point of the cell. In regions where the wave function $\psi_{\vec{k}}$ is small, a slight deviation of $\psi_{\vec{k}}$ from the exact value will lead to a large $\sigma_{II}(\vec{r})$. However, when calculating matrix elements, these regions generally are expected to give negligible contributions. Therefore, σ_{II} does not seem to be an appropriate measure. A more adequate criterion for the wave function seems to be the expectation value of the operator $(H-E)^2$. The natural generalization to cases where the highest derivatives of the wave function or the potential are discon-

TABLE II. Energies at Γ, E_Γ, and band widths ΔE for the highest core bands of Ni, Cu, and Al.

Metal	Ni		Cu		Al	
Corresp. atomic level	3s	3p	3s	3p	2s	2p
E_Γ (in Ry)	−6.9248	−4.2436	−8.3722	−5.4248	−7.0952	−4.2420
ΔE (in Ry)	0.006	0.02	0.002	0.01	0.0003	0.0018

continuous is the expression

$$\sigma_{III}^2 = [\int (H\psi_{\vec{k}})^*(H\psi_{\vec{k}})\,d\tau - E_{\vec{k}}^2 \int \psi_{\vec{k}}^* \psi_{\vec{k}}\,d\tau]/\int \psi_{\vec{k}}^* \psi_{\vec{k}}\,d\tau$$
$$\equiv \int |(H - E_{\vec{k}})\psi_{\vec{k}}|^2\,d\tau / \int \psi_{\vec{k}}^* \psi_{\vec{k}}\,d\tau \quad .$$

In column 4 of Table I, the values σ_{III}^2 are given for the same cases as considered above. It is remarkable that a rapid decrease of σ_{III}^2 is only achieved if the values of N and J are chosen in a well-balanced manner.

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