However, the spontaneous Hall coefficient is different from 0 up to the point $R/R_0 = 0.78$, and $\mathrm{H/Ni} = 0.85$. It means that in the region of the atomic ratio $0.6 < \mathrm{H/Ni} < 0.85$ weak ferromagnetism exists ($A_s > 0$). This fact corresponds to the x-ray data of Majchrzak,[10] on the basis of which the existence of the ferromagnetic α phase up to $\mathrm{H/Ni} = 0.85$ was proven. Figures 5 and 6 show relative values of A_0 and A_1 as functions of the atomic ratios H/Ni. The atomic ratios were taken from Ref. 3. The ordinary Hall coefficient's dependence on the atomic ratio H/Ni is similar to the earlier observed dependence in the Pd-H system, but the interpretation of this situation in the present case is more complicated. In the Ni-H system the ordinary Hall coefficient rapidly decreases at the atomic ratio $\mathrm{H/Ni} \approx 0.3$, whereas this decrease is observed in the Pd-H system for $\mathrm{H/Pd} = 0.83$.[11]

The measurements of Hall coefficients for pure Ni under high hydrostatic pressure (up to 20 kbar) using gasoline as a pressure medium have not shown changes of the ordinary Hall coefficient A_0 exceeding ± 2%; the extraordinary Hall coefficient A_1 decreases about 7%. The changes of spontaneous magnetization observed in our experiments will be discussed elsewhere.

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Plane-Wave–Gaussian Energy-Band Study of Nb

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The numerical accuracy of the plane-wave–Gaussian (PWG) mixed-basis method of calculating crystalline energy bands is displayed for Nb. Atomic studies involving the Gaussian basis and crystalline studies involving the PWG mixed basis are systematically developed to establish the dependence of the energy eigenvalues upon the number of Gaussians, the number of plane waves, and the Gaussian overlap parameter. Use of the Nb crystalline potential of Deegan and Twose allows comparison with their results.

I. INTRODUCTION

The purpose of this paper is to establish the quantitative validity of the plane-wave–Gaussian (PWG) mixed-basis set[1] for crystalline electron energy-band and wave-function calculations. To do this, the results of systematic studies are presented in order to establish the dependence of the energy eigenvalues upon the number of Gaussians, the number of plane waves, and the Gaussian overlap parameter in wave-function and potential expansions. The use of Deegan and Twose's[2] muffin-tin potential also allows comparison of PWG results with their results.

An earlier paper,[1] which introduced the PWG mixed basis, focused upon the excellent plane-wave convergence properties of this particular mixed-basis set. A future paper will present the self-consistent PWG formalism in which the crystalline PWG wave functions are used to calculate a new crystalline charge density, which, in turn, yields a new crystalline potential. This self-consistent formalism is simple, and the early computational results are very promising. How successful this particular mixed basis will be for total-energy calculations is not yet known, however.

The background of the PWG mixed-basis method is briefly as follows. Of the best-known techniques for mathematically describing crystalline electron wave functions, only the linear combination of atomic orbitals (LCAO) and the orthogonalized-plane-wave (OPW) methods are not oriented toward muffin-tin potentials. The most successful LCAO calculations[3] involve overlapping Gaussians centered upon the various atom sites. This pure Gaussian basis set is extremely efficient, and the method is very powerful. However, the extensive overlap of wave functions and potential from one atom site to the next results in a complicated formalism and in complex computer coding. The traditional OPW method[4] artificially divides electron states into "nonoverlapping" core states (whose wave functions are numerically tabulated over radial atomic meshes) and into valence and conduction states expressed in terms of plane waves orthogonalized to the core states. Plane-wave convergence can be poor[5]; the OPW method fails completely for crystals such as C, ZnO, Cu, and Nb. The rapid variations of the valence and conduction wave functions near atom sites are not adequately represented in the OPW basis until a prohibitively large number of plane-wave terms are included. By that time, overlap of the core states usually destroys the calculation anyway. Consequently, various mixed-basis set formalisms have been introduced which augment the OPW basis with suitably chosen nonoverlapping corelike functions.[2,6] These new functions were previously obtained by numerically integrating Schrödinger's equation over an atomic radial mesh, and then altering the large-r behavior of the function so as to avoid overlap with functions on neighboring sites. The mixed-basis method has been very successful.

The PWG method uses an analytic mixed basis for wave-function and potential expansions. The basis turns out to be so efficient that no distinction need be made between core, valence, and conduction states. As in the Kunz mixed-basis formalism, all electron energies are obtained from the same secular equation. In the Deegan-Twose mixed-basis formalism, core energies and wave functions were obtained from numerical mesh calculations, and valence and conduction energies and wave functions were obtained from an OPW-like secular equation. The PWG basis consists of plane waves and of almost nonoverlapping LCAO functions, each of which is expressed as a sum of Gaussians. The coefficient of each Gaussian can be determined by least-squares fitting atomiclike functions defined numerically over a radial mesh. Or, alternatively for the wave functions, one can use a Gaussian basis to minimize the energy in a spherically symmetrized potential. In both cases both interior and overlapping Gaussians should be used in determining the coefficients. The appreciably overlapping Gaussians are then discarded, leaving almost nonoverlapping analytic functions which correctly express the wave function or potential behavior near atom sites. The plane-wave part of the basis must then describe the longer-wavelength behavior. The plane-wave convergence of the basis is good. The analytic character of the basis functions is highly convenient and leads to a very simple formalism and to simple computer coding. The numerical accuracy of the PWG method is the subject of this paper.

In Sec. II the PWG formalism is presented to establish the concepts and working equations. Section III studies pure Gaussian expansions in the Nb atom. First a numerically tabulated potential is used. The wave functions are expanded in a Gaussian basis to study the energy eigenvalue dependence upon the number of Gaussians in the wave function basis. Then the potential is also expanded in a Gaussian basis to study the effect of this approximation upon the atomic eigenvalues. Having established the requirements upon the Gaussian basis for wave functions and potential, Sec. IV then examines the PWG mixed basis in the Nb crystal. The dependence of the crystalline energy eigenvalues upon the number of plane waves in the potential expansion is shown first. Eigenvalue convergence with respect to the number of plane waves in the wave-function basis is next displayed and compared to the results of Deegan and Twose. Finally, the influence on the eigenvalues of neglect of near-neighbor Gaussian wave-function overlap is examined. Section V then briefly summarizes the results of the paper.

II. PWG FORMALISM

Since Nb has one atom per crystalline unit cell, the present formalism will be presented for that case. The more general formalism is a trivial extension.[1]

The crystal potential is written

$$V(\vec{r})=\sum_\alpha V^\alpha \sum_a e^{-\alpha(\vec{r}-\vec{R}_a)^2}+\sum_{\vec{K}}\delta V_{\vec{K}}\, e^{-i\vec{K}\cdot\vec{r}}\,, \qquad (1)$$

where atom sites are at R_a, and the $\vec{K}$ sum is over reciprocal-lattice vectors.

The crystalline wave functions are written

$$\Psi^\mu(\vec{r})=\sum_{nlm} C^\mu_{nlm}\Big[\sum_a e^{i\vec{k}_0\cdot\vec{R}_a}\sum_\alpha A^\alpha_{nl}\, e^{-\alpha(\vec{r}-\vec{R}_a)^2} \times|\vec{r}-\vec{R}_a|^l\, Y^l_m(\vec{r}-\vec{R}_a)\Big] +\sum_{\vec{K}} B^\mu_{\vec{K}}\Big[e^{i(\vec{k}_0+\vec{K})\cdot\vec{r}}\Big]\,, \qquad (2)$$

where the PWG basis functions are in brackets, μ labels the particular electron state at k_0 in the Brillouin zone, and nlm are the usual atomic quantum numbers. Variational freedom is given to the B and C coefficients. The A^α_{nl} are predetermined from some spherically symmetrized atomlike problem.

It is very convenient to choose the set of α so that the Gaussians are even tempered[7]:

$$\alpha_i=\alpha_1(\alpha_s/\alpha_1)^{(i-1)/(s-1)}\,. \qquad (3)$$

The more physical Gaussian standard deviations σ_i, where

$$\alpha_i = 1/2\sigma_i^2 ,$$

are then also even tempered. This relationship corresponds closely to the familiar logarithmic radial mesh in atomic calculations.

The fattest "nonoverlapping" Gaussian α_s is chosen from the negligible overlap condition:

$$e^{-\alpha_s (R_{\text{nn}}/2)^2} = \tau , \tag{4}$$

where τ is called the overlap parameter and R_{nn} is the nearest-neighbor distance. Gaussians with a standard deviation smaller than σ_s will be called interior Gaussians. Ones with a larger standard deviation will be called overlapping Gaussians.

The construction and solution of the secular equation

$$\begin{aligned} H\psi &= \lambda U \psi , \\ H_{ij} &= (\varphi_i , \mathcal{H}\varphi_j) , \\ U_{ij} &= (\varphi_i , \varphi_j) , \end{aligned} \tag{5}$$

where the φ_i are the basis functions, is routine.[8] All matrix elements of H and U reduce to simple analytic functions in the PWG formalism.

The Gaussian coefficients V^α and A^α_{nl} can be chosen by least-squares fitting numerically tabulated atomlike functions with a Gaussian series. Merely choose D to minimize

$$S = \int r^2 dr \left(f(r) - \sum_{i=1}^{s+t} D_i e^{-\alpha_i r^2} \right)^2 , \tag{6}$$

where s interior and t overlapping Gaussians are used. Enough overlapping Gaussians should be used to adequately represent variations in the outer regions of f. Minimization of S with respect to the D_i results in the usual linear equations:

$$\int r^2 f(r) e^{-\alpha_i r^2} dr = \textstyle\sum_j D_j \int r^2 e^{-(\alpha_i + \alpha_j) r^2} dr . \tag{7}$$

If α_1 is not chosen by other considerations, it can be adjusted to minimize S [Eq. (6)] with the D_i determined by Eq. (7).

The other convenient method of determining the A^α_{nl} involves spherically symmetrizing the crystal potential about a lattice site and solving the secular equation (5) using the Gaussian basis

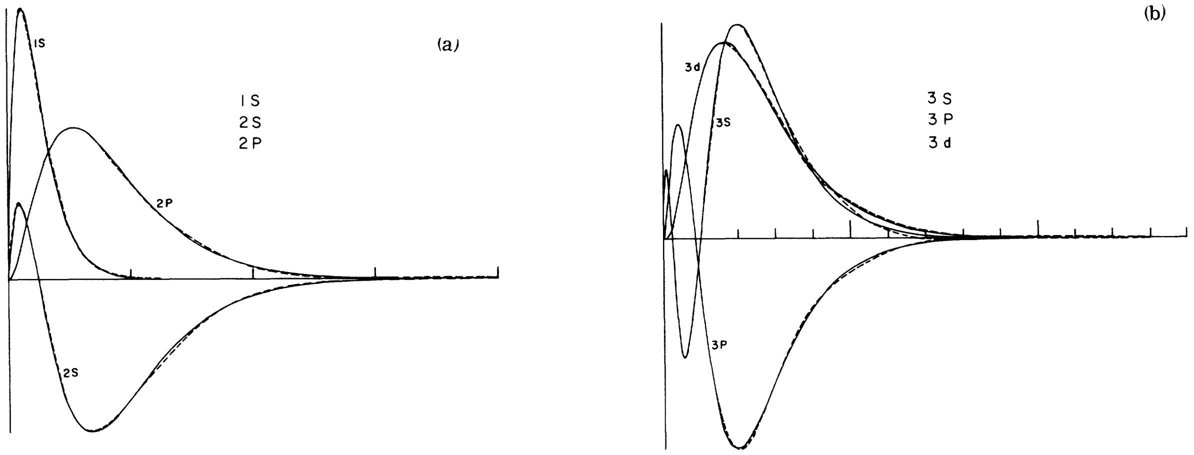
$$\{ r^l y^l_m(\theta, \varphi) e^{-\alpha_i r^2} \} \quad (i = 1, s+t) . \tag{8}$$

The A^α_{nl} are the eigenvectors of Eq. (5). Again, enough overlapping Gaussians must be used to span the outer region of V. The overlapping Gaussians are then dropped from the crystalline basis.

This prescription for choosing the LCAO nonoverlapping corelike functions is simple and easy to apply to unfamiliar atoms. No "operator intervention" is necessary in the very fast computer program that adjusts α_1 to minimize S [Eq. (6)]. The dropping of the overlapping Gaussians modifies the wave functions everywhere (small and large r), but the fat dropped Gaussians are easily simulated by the plane-wave part of the basis. This prescription is in contrast to that used by earlier mixed-basis methods in which the radial Schrödinger's equation is numerically integrated outward and joined continuously with continuous first derivative to an analytic polynomial or sine function which vanishes at half the nearest-neighbor distance. In that case, the plane-wave part of the crystal wave function must do no work in the small-r region, but must do substantial work in the large-r region. It is not clear *a priori* which prescription is best. Computer convergence studies must settle the

TABLE I. Atomic Nb Slater eigenvalues are given in Ry for a wave-function basis consisting of s interior Gaussians and t overlapping Gaussians. Integrals involving V_s were evaluated numerically over the Herman-Skillman radial mesh. The standard deviation of the smallest Gaussian σ_1 (given in a.u.) was adjusted for the best over-all fit. The Gaussian overlap parameter τ is 0.003. Herman-Skillman eigenvalues resulting from numerically integrating Schrödinger's equation with their SCHEO subroutine are given in the column headed HS.

s		16	12	8
t		5	5	4
σ_1	(HS)	0.002	0.008	0.018
1s	−1359.843	−1359.744	−1354.011	−1305.486
2s	−188.971	−188.961	−188.377	−183.307
2p	−174.351	−174.351	−174.350	−174.264
3s	−32.037	−32.035	−31.932	−31.015
3p	−26.353	−26.352	−26.352	−26.303
3d	−15.838	−15.838	−15.838	−15.817
4s	−4.377	−4.376	−4.359	−4.196
4p	−2.769	−2.769	−2.769	−2.754
4d	−0.394	−0.394	−0.394	−0.391
5s	−0.327	−0.327	−0.325	−0.311



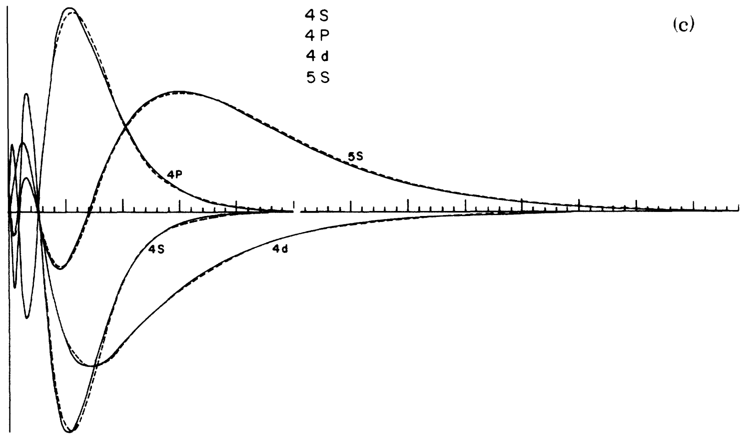


FIG. 1. Functions $r\,\psi_{nl}(r)$ were calculated with the Slater-exchange atomic potential. The solid lines represent three functions which cannot be distinguished to the accuracy of the figure: the numerical Herman-Skillman solutions, the 12-interior (and 5-overlapping) Gaussian fit, and the 16-interior (and 5-overlapping) Gaussian fit. The dashed lines show the 8-interior (and 4-overlapping) Gaussian fit. The horizontal axis shows the radial distance with small hash marks every 0.2 a.u. Half the nearest-neighbor distance is 2.7 a.u.

question.

III. ATOMIC GAUSSIAN EXPANSION

Niobium is a transition metal with an atomic configuration of $(4d)^4(5s)^1$ outside of closed shells. Deegan and Twose tabulate a muffin-tin potential for the Nb crystal.[9] We will refer to this potential as $V_{\rm DT}$. When this potential is used as an isolated-atom potential, the $4d$ and $5s$ states have a positive energy and are thus not bound. Consequently, in the first atomic study, where the emphasis is upon the upper states, the very similar Slater-exchange Nb potential V_S will be used. This potential can be obtained by use of the well-known Herman-Skillman atomic computer programs.[10] The lower eigenvalues are very similar for the two potentials, while the upper $4d$ and $5s$ states are bound in the Slater potential.

This first study is concerned with atomic Gaussian wave-function expansions. We want to determine atomic-energy eigenvalues by using an even-tempered Gaussian basis (8) in the atomic variational problem (5). How many Gaussian basis functions must be used to obtain eigenvalues for the upper Nb states which are correct to 0.001 Ry? To answer this question the Herman-Skillman programs were run to self-consistency with Slater's exchange. The resulting eigenvalues are taken as correct. The atomic potential was extracted for use in (5). Gaussian matrix elements of this potential were then evaluated by numerical integration over the Herman-Skillman atomic radial mesh. The secular equation (5) was solved with three separate numbers of interior Gaussians. For each interior Gaussian set, enough overlapping Gaussians of the same even temper (3) were used to span the region of variation of V. (When sufficient overlapping Gaussians are used, the bound-state eigenvectors will contain vanishing amounts of the last few Gaussians.) The outermost interior Gaussian was chosen with an overlap value of 0.003 [Eq. (4)]. The standard deviation of the smallest Gaussian was then adjusted to give the best eigenvalue fit. The results are tabulated in Table I. It is clear from the table that eight interior Gaussians are inadequate for high-precision computations, while 16 interior Gaussians are more than adequate for a precision of 0.001 Ry in the upper states.

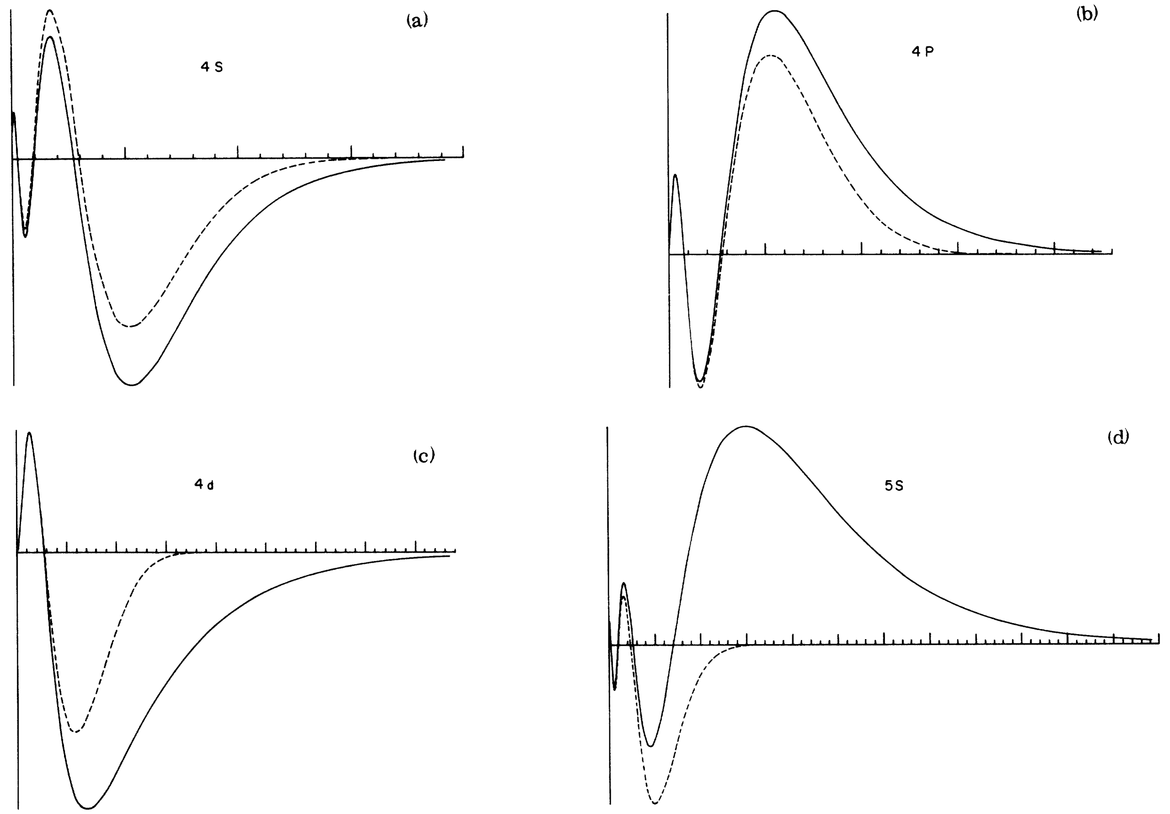


FIG. 2. Solid functions $r\,\psi_{nl}(r)$ were calculated with the Slater-exchange atomic potential with 16-interior (and 5-overlapping) Gaussians. The dashed functions are obtained by summing only over the 16 interior Gaussians. These dashed functions are then used as PWG LCAO basis functions. Only the 4*s* thru 5*s* functions are shown since the 1*s* thru the 3*d* dashed functions cannot be distinguished on the scale of the figure from the solid functions. The horizontal axis shows the radial distance with small hash marks every 0.2 a.u. Half the nearest-neighbor distance is 2.70 a.u.

The energies obtained with 12 interior Gaussians are already very good.

The Herman-Skillman Slater-exchange wave functions multiplied by r and the corresponding functions obtained from eight interior Gaussians are displayed in Fig. 1. The functions obtained

TABLE II. Atomic Nb Deegan-Twose eigenvalues are given in Ry. The potential V_{DT} is approximated by s interior Gaussians and t overlapping Gaussians. The potential overlap parameter is 0.001. The standard deviation of the smallest Gaussian σ_1 (in a.u.) was obtained by minimizing S[(Eq. (6)] in the potential fit. The wave-function Gaussian basis consists of 16 interior Gaussians and 5 overlapping Gaussians with a wave-function overlap parameter of 0.003, and a smallest Gaussian standard deviation of 0.002 a.u. The eigenvalues in the first two columns were obtained from a numerically tabulated V_{DT}. For the column headed HS, the Herman-Skillman subroutine SCHEO was used to numerically integrate Schrödinger's equation. For the column headed V_{mesh}, the wave-function Gaussian basis was used, but integrals involving V_{DT} were performed over a numerical Herman-Skillman mesh.

s			21	16	11	9
t			10	5	5	5
σ_1	(HS)	(V_{mesh})	0.0011	0.0009	0.0009	0.0009
1*s*	−1358.538	−1358.436	−1358.436	−1358.419	−1358.462	−1358.133
2*s*	−187.652	−187.641	−187.641	−187.639	−187.606	−187.711
2*p*	−173.031	−173.031	−173.031	−173.031	−172.992	−173.069
3*s*	−30.716	−30.715	−30.714	−30.717	−30.593	−30.490
3*p*	−25.032	−25.032	−25.032	−25.033	−24.943	−24.829
3*d*	−14.517	−14.517	−14.517	−14.518	−14.490	−14.387
4*s*	−3.091	−3.091	−3.091	−3.094	−3.110	−2.996
4*p*	−1.498	−1.498	−1.498	−1.500	−1.500	−1.415

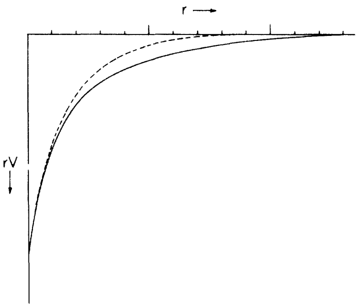


FIG. 3. Solid function shows $rV(r)$ for the Deegan-Twose muffin-tin potential. The numerical tabulation of Deegan and Twose coincides on the scale of the figure with the 21-interior (and 10-overlapping) Gaussian fit. The dashed function shows the sum over only the 21 interior Gaussians. This function is the Gaussian contribution to Eq. (1). The horizontal axis shows the radial distance with small hash marks every 0.2 a.u. Half the nearest-neighbor distance is 2.70 a.u.

from 12 and 16 interior Gaussians cannot be distinguished on the figure from the Herman-Skillman functions. The agreement is excellent from the very tightly bound 1s state to the very loosely bound 5s state. The even temper (3) allows the Gaussians to effectively span this large range. In further studies in this paper, 16 interior Gaussians will be used for wave-function expansions. One can expect a numerical uncertainty of less than 0.001 Ry with this expansion.

Figure 2 shows the free-atom (Slater-exchange) wave functions multiplied by r along with the functions obtained by dropping the overlapping Gaussians. These last functions will be the LCAO basis functions in the PWG calculations. Only the 4s through the 5s functions are shown since the contribution of the overlapping Gaussians to the lower states is too small to be seen on the figures. The 5s basis function has lost its outer node, but the behavior close to the nucleus is still strongly 5s-like. The other basis functions also retain their atomic character around the nucleus, but they are modified at larger distances.

TABLE III. The Fourier transforms of the Deegan-Twose crystal potential $V(K)$, of the Gaussian portion [see Eq. (1)] $V_G(K)$, and of the remaining plane-wave portion $\delta\ V(K)$ are shown as a function of the total number of plane waves up to that point in the plane-wave expansion. For the Gaussian fit, 21 interior Gaussians were used with a potential overlap parameter of 0.001 and a smallest Gaussian standard deviation of 0.0011 a.u. The rows do not always add up perfectly because of rounding errors.

N PW	$V(K)$	$V_G(K)$	$\delta V(K)$
1	−1.6934	−0.8072	−0.8862
13	−1.1082	−0.6862	−0.4220
19	−0.7768	−0.5901	−0.1867
43	−0.5884	−0.5133	−0.0751
55	−0.4782	−0.4515	−0.0267
79	−0.4098	−0.4014	−0.0084
87	−0.3632	−0.3604	−0.0028
135	−0.3283	−0.3266	−0.0017
141	−0.3000	−0.2984	−0.0016
177	−0.2760	−0.2747	−0.0013
201	−0.2553	−0.2546	−0.0007
225	−0.2374	−0.2373	−0.0000
249	−0.2219	−0.2224	0.0006
321	−0.2085	−0.2094	0.0009
369	−0.1870	−0.1878	0.0008
381	−0.1782	−0.1787	0.0004
429	−0.1704	−0.1705	0.0001
459	−0.1632	−0.1630	−0.0002

We have thus established that 16 interior Gaussians are adequate for the wave-function basis. We can now use this wave-function basis to examine Gaussian fits to the Deegan-Twose potential for Nb. This study is especially interesting because the even-tempered Gaussian series must try to simulate the $1/r$ singularity in the potential. How well can this be done? To answer this question, eigenvalues will be obtained in three ways: The most

TABLE IV. Nb crystalline Γ-point eigenvalues in Ry are given where various numbers of plane waves (N pw) are used in the Gaussian plane-wave expansion of the Deegan-Twose potential [Eq. (1)]. The states are labeled by their degeneracy (Deg.). The potential Gaussian fit involved 21 interior Gaussians with a potential overlap parameter of 0.001 and a smallest Gaussian standard deviation of 0.0011 a.u. The wave-function basis consisted of 55 plane waves and 16 interior Gaussians with a wave-function overlap parameter of 0.003 and a smallest Gaussian standard deviation of 0.002 a.u. The Slater atomic potential was used for the determination of the wave-function Gaussian basis. The ten lowest states, 1s through 5s, were used in the basis.

	N pw						
Deg.	459	369	321	177	135	87	55
1	−3.107	−3.107	−3.107	−3.107	−3.109	−3.112	−3.111
3	−1.457	−1.457	−1.458	−1.459	−1.460	−1.463	−1.466
1	0.322	0.322	0.322	0.322	0.322	0.323	0.328
3	0.761	0.761	0.760	0.759	0.758	0.759	0.744
2	0.932	0.932	0.931	0.929	0.932	0.928	0.939
3	1.812	1.812	1.812	1.812	1.812	1.812	1.814

TABLE V. Plane-wave convergence of Nb crystalline eigenvalues (in Ry) at Γ (0, 0, 0), H (1, 0, 0), and $P(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the Brillouin zone. Columns are headed by the number of plane waves included in the wave-fucntion basis. The column headed DT gives the best values obtained by Deegan and Twose. The DT number in parenthesis was estimated from a figure rather than from a Table. The crystalline potential was expressed by 459 plane-wave terms and 21 interior Gaussians with a potential overlap parameter of 0.001 and a smallest Gaussian standard deviation of 0.0011 a.u. The wave-function Gaussian basis was derived from the Slater atomic potential 1s thru 5s states. Sixteen interior Gaussians were used, with a wave-function overlap parameter of 0.003 and a smallest Gaussian standard deviation of 0.002 a.u. States are labeled by their crystalline degeneracy (Deg.). The column headed 79-16 gives eigenvalues when the potential consisted of 459 plane waves and 16 interior Gaussians with a potential overlap of 0.001 and a smallest Gaussian standard deviation of 0.0009 a.u. Seventy-nine plane waves were used in the wave-function basis.

				Γ				
Deg.	DT	79	55	43	19	13	1	79-16
1	−3.106	−3.107	−3.107	−3.107	−3.106	−3.104	−3.072	−3.106
3	(−1.46)	−1.457	−1.457	−1.456	−1.452	−1.441	−1.286	−1.456
1	0.318	0.322	0.322	0.322	0.322	0.322	0.338	0.322
3	0.758	0.760	0.761	0.765	0.788	0.788	1.486	0.760
2	0.932	0.931	0.932	0.934	0.951	1.032	1.487	0.931

				H	
Deg.	DT	68	38	14	6
1		−3.073	−3.073	−3.072	−3.064
3	−1.517	−1.519	−1.518	−1.504	−1.470
2	0.434	0.433	0.435	0.469	0.469
3	1.106	1.102	1.105	1.162	1.486
3	1.406	1.420	1.426	1.433	1.491

				P			
Deg.	DT	80	68	44	28	16	4
1		−3.085	−3.085	−3.085	−3.085	−3.083	−3.071
3	−1.502	−1.504	−1.504	−1.504	−1.502	−1.492	−1.427
3	0.645	0.640	0.640	0.641	0.645	0.665	0.778
2	0.998	0.998	0.998	1.001	1.013	1.031	1.487
1		1.509	1.511	1.515	1.519	1.521	1.610
3	1.563	1.567	1.568	1.573	1.579	1.615	1.869

accurate method is to use the Herman-Skillman differential equation subroutine SCHEO on the numerically tabulated Deegan-Twose Nb potential (numerical wave function − numerical potential). One can also use the Gaussian wave-function basis (8) in Eq. (5) and obtain potential matrix elements by numerical integration (Gaussian wave function − numerical potential). Or, finally, one can least-squares fit the potential with an even-tempered Gaussian series. The combined use of a Gaussian wave-function basis and a Gaussian representation for the potential (Gaussian wave function − Gaussian potential) results in analytic matrix elements in Eq. (5). Comparison of the resulting eigenvalues should then show up relative inadequacies in Gaussian representations for wave functions and for potentials. In the Gaussian fit to the potential, the potential overlap parameter τ [Eq. (4)] was chosen to be 0.001. The standard deviation of the smallest Gaussian was adjusted in each case to minimize S [Eq. (6)].

The resulting Nb eigenvalues are given in Table II. It can be seen that all eigenvalue differences (to 0.001 Ry) between the Gaussian potential and the numerically tabulated potential have disappeared when 21 interior Gaussians are used in the potential expansion. Differences are very small when 16 interior Gaussians are used. Comparison of the first three columns shows that once a Gaussian wave-function basis is introduced no further harm is done by using a Gaussian representation for the potential. The $1/r$ singularity can be adequately simulated by an even-tempered Gaussian series comprised of 21 interior Gaussians.

The function $rV_{\mathrm{DT}}(r)$ is plotted in Fig. 3 together with the function obtained by dropping the overlapping Gaussians. The latter function is the one used in Eq. (1). The sum of interior and overlapping Gaussians lies directly on top of the numeric function, except very close to the nucleus where large oscillations occur. We have seen that these oscillations do not appreciably affect the energy eigenvalues when a Gaussian wave-function basis is used.

IV. CRYSTALLINE PWG CALCULATIONS

The crystalline calculations will use the same lattice constant as Deegan and Twose, namely, the bcc lattice constant is taken to be 3.30A.

TABLE VI. Plane-wave convergence of Nb crystalline eigenvalues at Γ when the Gaussian wave-function basis is derived from the 13 atomic states 1*s* through 6*s*. Sixteen interior Gaussians are used with an overlap parameter of 0.003 and a smallest Gaussian standard deviation of 0.002 a.u. The crystal potential consisted of 459 plane-wave terms with 21 interior Gaussians. The potential overlap is 0.001 and the smallest Gaussian standard deviation is 0.0011 a.u. The column headings give the number of plane waves in the wave-function basis. For the subtable labeled V_{DT}, the atomic potential used in the Gaussian wave-function determination was the Deegen-Twose muffin tin, while the subtable headed V_{sl} used the Slater atomic potential. The column headed Deg. gives the degeneracy of the crystalline states.

			V_{DT}			
Deg.	79	55	43	19	13	1
1	−3.108	−3.108	−3.108	−3.108	−3.107	−3.092
3	−1.460	−1.458	−1.458	−1.457	−1.454	−1.392
1	0.322	0.322	0.322	0.322	0.322	0.331
3	0.760	0.761	0.763	0.769	0.769	1.267
2	0.930	0.930	0.931	0.935	0.967	1.268

			V_{sl}			
Deg.	79	55	43	19	13	1
1	−3.108	−3.108	−3.108	−3.108	−3.107	−3.092
3	−1.458	−1.457	−1.457	−1.457	−1.453	−1.381
1	0.322	0.322	0.322	0.322	0.322	0.331
3	0.760	0.761	0.763	0.769	0.769	1.268
2	0.930	0.930	0.931	0.935	0.967	1.268

Taking the 21-interior-Gaussian fit to the Deegan-Twose muffin-tin potential, we can determine the plane-wave coefficients of the potential expansion [Eq. (1)]. The total Fourier potential coefficient (evaluated by numerical integration), the Gaussian contribution (evaluated analytically), and the remaining plane-wave contribution are all tabulated in Table III. The basic idea behind the plane-wave–Gaussian mixed basis is strikingly illustrated. The plane-wave contribution is relatively large at low-K values, but the Gaussian terms completely dominate the higher-K small-wavelength region.

The first question to be studied concerns the number of plane-wave terms that must be kept in the potential expansion [Eq. (1)]. Table IV shows Γ point valence- and conduction-band eigenvalues as a function of the number of plane-wave terms in the potential expansion. Although the rest of our calculations will be done with 459 plane-wave terms, little would be lost (0.002 Ry) if only 177 plane waves were used.

Table V shows Γ, H, and P valence- and conduction-band eigenvalues for various numbers of plane waves in the wave-function expansion [Eq. (2)]. The best Deegan-Twose energies are also included for comparison. The agreement between the PWG eigenvalues computed with 79 plane waves in the wave-function basis and the Deegan-Twose energies computed with about 180 plane waves is very good. Plane-wave–Gaussian plane-wave convergence of the eigenvalues is, on the whole, more rapid than that of Deegan-Twose for Nb. It is not known if the PWG prescription for picking pseudocore basis functions is generally better than that of other mixed-basis methods.

Table V also shows PWG eigenvalues when only 16 interior Gaussians, rather than 21, are used in the potential expansion. Clearly the differences (0.001 Ry) are negligible.

One of the advantages of solving the secular equation (5) with the atomic Gaussian basis (8) to obtain the contracted Gaussian coefficients A^{α}_{nl} is that positive energy wave functions can be obtained. Thus the contracted Gaussian basis set can simulate correctly the small-r behavior of states which are empty in the isolated atom. Plane-wave–Gaussian eigenvalue convergence is presented in Table VI for the case where 5*p*-, 5*d*-, and 6*s*-like basis functions are added to the basis set. Plane-wave convergence is seen to be slightly improved, with the functions obtained from the Deegan-Twose atomic potential slightly superior to those obtained from the Slater potential. Since the crystal potential is comprised of Deegan-Twose muffin tins, this is not unexpected.

The last numerical study examines the effect of neglecting Gaussian overlap from site to site. Does this overlap have a strong influence on the PWG eigenvalues? To examine this question, the wave-function overlap parameter was stepped from 0.003 to 0.01. The resulting Γ point eigenvalues are shown in Table VII. The most striking effect is that the determinant of the orthogonality matrix U [Eq. (5)] goes negative at a smaller and smaller number of plane waves as the overlap parameter becomes larger. Of course, if the determinant of U were correctly calculated from Eq. (5), taking overlap into account, the determinant would remain positive definite. The neglect of near-neigh-

TABLE VII. Convergence of Nb crystalline Γ-point eigenvalues in Ry for several values of the wave-function Gaussian overlap parameter τ. Ten Gaussian basis functions derived from atomic states 1*s* through 5*s* were determined from Slater's atomic potential. Sixteen interior Gaussians were used with a smallest Gaussian standard deviation of 0.0038 a.u. The potential is represented by 459 plane-wave terms and 21 interior Gaussians with a overlap of 0.001 and a smallest Gaussian standard deviation of 0.0011 a.u. The entry $|U|<0$ means that the determinent of the orthogonality matrix U [Eq. (5)] is negative. The column headed Deg. labels the degeneracy of the crystalline states.

			$\tau=0.005$			
Deg.	79	55	43	19	13	1
1	$\|U\|<0$	−3.106	−3.106	−3.106	−3.104	−3.088
3		−1.459	−1.458	−1.457	−1.451	−1.346
1		0.323	0.323	0.323	0.323	0.332
3		0.764	0.766	0.780	0.780	1.371
2		0.930	0.931	0.941	0.997	1.372

			$\tau=0.007$		
Deg.	55	43	19	13	1
1	$\|U\|<0$	−3.105	−3.105	−3.104	−3.094
3		−1.460	−1.460	−1.456	−1.380
1		0.323	0.323	0.323	0.330
3		0.769	0.778	0.778	1.301
2		0.929	0.935	0.977	1.302

			$\tau=0.009$	
Deg.	43	19	13	1
1	$\|U\|<0$	−3.104	−3.104	−3.097
3		−1.462	−1.460	−1.401
1		0.324	0.324	0.329
3		0.778	0.778	1.252
2		0.931	0.963	1.252

			$\tau=0.01$	
Deg.	43	19	13	1
1	$\|U\|<0$	−3.104	−3.103	−3.097
3		−1.463	−1.461	−1.409
1		0.324	0.324	0.329
3		0.779	0.779	1.232
2		0.929	0.958	1.232

bor overlap of the Gaussians leads to an incorrect evaluation of Eq. (5), which leads to the negative determinant. The same negative determinant was encountered earlier in OPW calculations and was there traced to neglect of the very small overlap of the OPW core states.[11] It occurred in OPW calculations between roughly 400 and 1000 plane waves. It occurs much earlier in PWG. Thus the neglect of Gaussian overlap from atom site to atom site has catastrophic consequences if too many plane waves are used. However, immediately before the catastrophe, the PWG eigenvalues are still reasonable, as can be seen in Table VII. OPW experience also confirms the fact that the eigenvalues level off at reasonable values as more and more plane waves are added to the wave-function basis, and then abruptly plunge as the determinant of U goes negative. One must simply stay well away from the edge to obtain very reliable results. The overlap parameter must, however, be kept in mind when doing PWG calculations.

V. CONCLUSIONS

Gaussian basis sets do a very good job both for wave-function expansions and for potential expansions for all but the deepest core states. For Nb, "very good" means an eigenvalue accuracy of 0.001 Ry. Sixteen interior Gaussians for the wave-function expansion and 21 interior Gaussians for the potential produce high-quality results.

The even-tempered Gaussian series coupled with the plane-wave series form a very effective mixed-basis set for crystalline wave functions and potentials. This effectiveness is most vividly illustrated quantitatively in Table III and pictorally in Fig. 2.

The resulting Nb eigenvalues converge rapidly at a small number of plane waves. They are relatively insensitive to the neglect of Gaussian overlap from site to site. They are in remarkably close agreement with the results of Deegan and

Twose.

We thus conclude that high-precision crystalline calculations are feasible with the PWG method of calculating energy bands.

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Volume Change Associated with Noncubic Defects in a Monatomic Lattice*

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The formalism of the method of lattice statics is applied to obtain an expression for the volume change associated with a noncubic point defect in a monatomic lattice, assuming that the defect exerts no shear stress. This expression is used to calculate the volume changes associated with the octahedral and tetrahedral carbon interstitials in α-iron.

One of the physically interesting changes in the properties of a crystal brought about by the introduction of a point defect into the lattice is the volume change, or dilatation induced by the relaxation of the atoms of the host crystal to new equilibrium conditions. Currently, the most common method of calculating the dilatation associated with a given defect is to treat a portion of the crystal as an elastic continuum and obtain the strength parameter of the defect by somehow matching the displacements of host atoms in a discrete "core" region near the defect to the displacements of the atoms along the boundary between the discrete region and continuum region of the crystal.

More recently, a completely atomistic approach has been applied to the problem of determining the properties of point defects[1–4] in crystals. This technique, known as the method of lattice statics, is unique in that the equations of elasticity theory can be obtained directly from the corresponding lattice-statics equations for points in the lattice far away from the defect. Hardy[5] has shown that this natural transition from lattice theory to elasticity theory can be used to obtain a consistent expression for the lattice-strength tensor G_{ij} which is used to represent the point defect as a singularity in the body force on the elastic medium:

$$-F_i = -\sum_j G_{ij} \frac{\partial}{\partial x_j} \delta(\vec{r}) , \tag{1}$$

where i and j are Cartesian-coordinate indices. In terms of the force $\vec{F}^l$ exerted by the defect on its lth neighboring atom and the position vector $\vec{R}^l$ of the lth atom in the perfect lattice, the strength tensor is

$$G_{ij} = \sum_l F_i^l R_j^l . \tag{2}$$

In the case of a cubic point defect, $G_{ij} = 0$ for $i \neq j$ and all of the diagonal elements, G_{ii} are equal to the same constant G. Hardy[5] has shown that for this case the dilatation Δv produced by the defect is

$$\Delta v = \frac{G}{K} = \sum_l \frac{F_i^l R_i^l}{K} , \tag{3}$$

where K is the bulk modulus of the host crystal.

The derivation given by Hardy can be extended