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Local pseudopotential theory for transition metals

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A simple *local*-pseudopotential formalism capable of describing d-band metals is introduced. The theory involves a straightforward method for generating a local pseudopotential for both valence *and* outermost-core-shell electrons. Niobium is used as a prototype to demonstrate the applicability of this method. Excellent agreement with nonlocal self-consistent pseudopotential and augmented-plane-wave band structures is obtained using a modest number of plane waves. The electronic density of states and core $4p$ absorption spectra are calculated. Two regions of distinctly different electronic character in the density of states could be demonstrated.

I. INTRODUCTION

We present the first self-consistent-pseudopotential[1-3] formalism capable of describing the electronic structure of d-band metals using simple *local* potentials. As an example, the method is applied to study the electronic structure of Nb, which has been studied extensively in the literature by different theoretical approaches.[4-14] Niobium is of particular interest because of the high transition temperatures of several superconducting Nb compounds. In recent years the use of pseudopotentials in calculations of the optical and electronic properties has become increasingly important and widespread. The basic concept behind pseudopotentials is the replacement of the actual potential describing all the electrons of an atom with a much weaker potential describing only its valence electrons.[15,16] This approach is very useful because it is the valence electrons which are responsible for the physical and chemical properties of solids. The weak nature of the potential permits the expansion of the crystalline wave function in terms of plane waves. This facilitates the calculation of valence charge densities and simplifies the extension of pseudopotential band calculations to self-consistency. Consequently, pseudopotentials can easily be applied to the study of crystals with large and complicated unit cells, e.g., vacancies, surfaces, and interfaces.[17,18] The main advantages of the pseudopotential approach over first-principles methods, particularly where self-consistency is required, are calculational simplicity, resulting in low computational expenses, and the availability of the crystalline wave functions which are necessary to obtain optical spectra and charge densities. The drawbacks of this approach, however, are the nonuniqueness of the generally highly parametrized model pseudopotential and the nonlocality required to apply the pseudopotential concept to d-band metals. In the following, we present a method to generate pseudopotentials which overcomes both of these difficulties. This is important because there has been much interest recently in the application of pseudopotentials to simple d-band metals and structurally more complicated transition-metal systems.[19-26]

II. THEORY

The basic concept underlying our method is to include the outermost s and p core electrons in addition to the customary d and s valence electrons. The method thus provides a description of the *complete* outer (valence) shell. Therefore, we need only deal with a local potential. A general and systematic procedure for generating this potential is given as follows. Beginning with a self-consistent $X\alpha$ atomic potential[27,28] using local Slater $\rho^{1/3}$ exchange, the screening potential due to the outer-shell electrons screening themselves is subtracted out. The resulting potential, hereafter referred to as the base potential, rapidly approaches the Coulomb potential of the respective ion outside the core although it still contains the effects of the mutual screening of the core and valence electrons. This base potential then is "pseudized" by multiplying it with a smooth steplike function

$$f(r;\lambda,r_c)=\frac{1-e^{-\lambda r}}{1+e^{-\lambda(r-r_c)}}\,, \qquad (1)$$

where r_c is the core radius and λ a reciprocal length characterizing the smoothness of the step function. This correctionfunction sets the potential almost to zero inside the core radius but leaves the base potential essentially unchanged outside.[29]

Varying the parameters r_c and λ the (atomic) eigenvalues of the fully screened ion pseudopotential are fit to the valence levels of the self-consistent $X\alpha$ calculation which are known to give very good agreement with experimental term values. The *same* set of fitted parameters then reproduces the atomic wave function and the valence energies and wave functions of the different possible ionic configurations as compared to the $X\alpha$ calculations of these configurations. As illustrated in Table I for Nb this is achieved to a high degree of accuracy. In fact, outside the core region the pseudo wave functions are almost indistinguishable from the $X\alpha$ wave functions (Fig. 1). The same good agreement still holds if one applies transition-state[27] theory to both the full atom and the pseudoatom. We have applied the method also to Au($r_c = 0.60415$ a.u., $\lambda = 11.41351$ a.u.$^{-1}$ for $\alpha = 0.69301$) and arrived at a pseudopotential displaying the same characteristics as described in the case of niobium. The method is suitable for the treatment of atoms which do not belong to the transition metals.[30]

We note that to a good approximation the core radius r_c can be chosen *a priori* halfway between the charge-density maxima of valence shell and outermost core shell. We find that in the fitting process the variations of r_c are restricted to ~±10% of this predetermined value. By keeping r_c fixed and varying only λ we can obtain only one possible good fit. This drastically reduces the degree of arbitrariness usually found in the highly parameterized model pseudopotentials. Hence, the resulting pseudopotentials seem to be almost unique and this close to first principles.

III. APPLICATION TO NIOBIUM

To demonstrate the applicability of our method to transition metals we have applied it to the calculation of the electronic structure of Nb. The band structure and the density of states (DOS) of this material have recently been investigated with several different theoretical approaches.[4-14] The results of these calculations are very similar and suggest that the influence of self-consistent screening in the crystal is unimportant. We have therefore calculated a band structure for niobium using only a superposition of self-consistent *atomic* pseudopotentials. With these atomic potentials (as described in Table I and Fig. 1) we obtain a band structure agreeing with those of an APW[6] and a self-consistent-nonlocal-pseudopotential (SCNLP)[4] calculation to within 0.5 eV.

We employed a basis set similar to that of the SCNLP calculation of about 80 plane waves and included the effects of 380 more plane waves through Löwdin perturbation theory.[31] Convergence tests showed that the 5s-, 4d-, and 4p-like bands were stable with this basis set. The deep 4s band, however, requires 180 plane waves to converge.

TABLE I. Comparison of pseudopotential eigenstates ($\alpha = 1$) with Herman-Skillman eigenstates ($\alpha = 1$) and experimental term values. The pseudopotential parameters are $r_c = 0.702\,70$ a.u. and $\lambda = 16.385$ a.u.$^{-1}$ resulting in a potential with minimum of -28.57 Ry at 0.86 a.u.

	Energy (Ry)			WFM[a]		r_m (a.u.)[a]	
	Pseudo	$X\alpha$[b]	Exp.[c]	Pseudo	$X\alpha$[b]	Pseudo	$X\alpha$[b]
				Atom			
4s	4.448	4.435	···	1.09	1.08	1.06	1.04
4p	2.811	2.827	···	1.02	1.00	1.14	1.10
4d	0.465	0.448	···	0.764	0.752	1.45	1.41
5s	0.396	0.402	···	0.546	0.548	3.14	3.10
				4^+ Ion			
4d	3.601	3.682	3.63	0.887	0.877	1.35	1.29
5s	2.920	2.985	2.95	0.741	0.741	2.48	2.40
5p	2.460	2.534	2.45	0.699	0.699	2.77	2.69
5d	1.796	1.850	1.71	0.622	0.622	3.51	3.43
6s	1.632	1.662	1.56	0.583	0.583	4.66	4.58

[a] Maximum of radial eigenfunction $P(r_m) = |R(r_m)|\, r_m$; cf. Ref. 28.

[b] Reference 28.

[c] Table I in Ref. 4 and references therein.

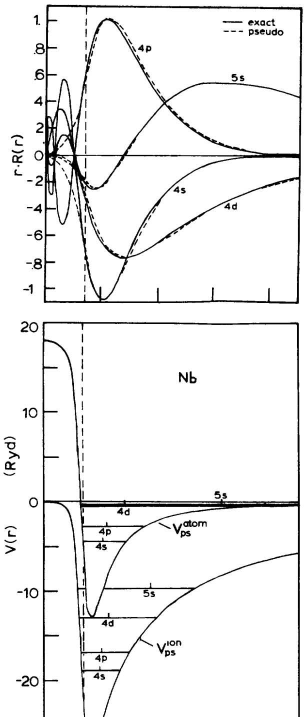

FIG. 1. Top: Comparison of radial eigenfunctions $rR_{nl}(r)$ of full Nb atom and Nb pseudoatom. Bottom: Nb^{13+} ion pseudopotential (V_{ps}^{ion}) and self-consistently screened pseudopotential of the Nb atom (V_{ps}^{atom}). The horizontal lines in the potentials indicate the respective eigenenergies. On these energy levels the maxima of $rR_{nl}(r)$ are marked by vertical bars.

Since the 4*p* core band is already a bonus for a pseudopotential calculation we chose to limit our investigation to the 4*p*, and 5*s* electrons.

In Fig. 2 and in the upper part of Fig. 3 we show the calculated DOS and compare it to the results of APW[6] and SCNLP.[4] We can distinguish three regions. Firstly, we see a three peak structure around −31.5 eV arising from the 4*p* core bands. Its width (1.45 eV) compares favorably with the results of self-consistent augmented-plane-wave[11] (APW) (1.63 eV, $\alpha=\frac{2}{3}$) and modified orthogonal-plane-wave[5] (OPW) (1.36 eV) calculations. Moreover, recent photoemission measurements[32] on Nb_2Ge place the 4*p* electrons, with comparable width, at the same energy below the Fermi level as we obtain from our calculation.

The second region in the DOS comprises the structures between −5 and 6 eV originating from the 4*d* and 5*s* electrons. They appear to be bonding-/antibonding-like split with the minimum at 1 eV above E_F as the center. We find this part of the DOS and the position of the Fermi energy in particular to be in excellent agreement with the results from APW[6] and SCNLP[4] displayed in the insets. A third region in the DOS becomes apparent in the upper part of Fig. 3. Above 6 eV the general form of the density of states takes on a free electron characteristic, but exhibits strong superposed structure.

Experimental information about the unfilled portions of the density of states can be obtained from core absorption and reflectivity spectra. Weaver *et al.*[33] have measured the reflectivity of Nb for photon energies up to 36.4 eV. They find a broad peak around 36 eV which is interpreted as arising from the 4*p* core levels.

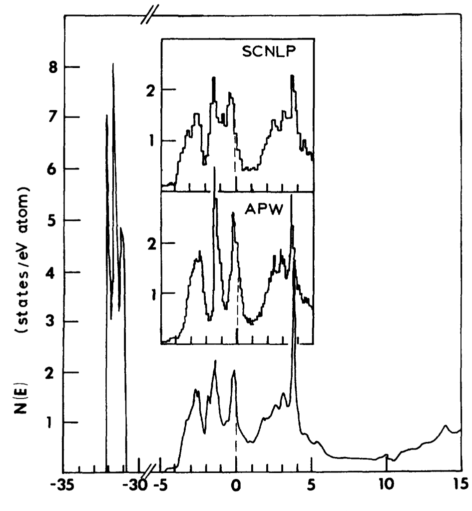

FIG. 2. Density of states between −35 and 15 eV compared to the results of APW (Ref. 6) and SCNLP (Ref. 4).

Since our pseudopotential approach describes the 4*p* core levels, we can straightforwardly calculate spectra involving transitions from these core states into states above the Fermi level. We have calculated the partial joint density of states $J(E)$ (Ref. 34) and partial imaginary part of the dielectric function $\epsilon_2(E)$ for such transitions (Fig. 3). As can be seen from a comparison of partial $J(E)$ and $N(E)$ in Fig. 3, the joint density of states closely follows the DOS.

Taking into account matrix element effects, we find that $\epsilon_2(E)$ exhibits a strong maximum at 32.4 eV, then decays rapidly to almost zero at 40 eV and shows no appreciable change up to 80 eV. We identify this maximum with the structure of the same height at about 36 eV in the $\epsilon_2(E)$ spectrum derived from reflectivity measurements. The sharp peak at 35.5 eV is due to transitions in the vicinity of N. The matrix element induced behavior of $\epsilon_2(E)$ for photon energies above 40 eV signifies the distinct character of the states in the third region of the DOS. The very weak matrix elements suggest a free-electron-like nature for the levels between 10 and 50 eV. It is important to note that because of the narrowness of $\epsilon_2(E)$ 4*p* core absorption spectra should have an almost identical shape.

IV. SUMMARY

In summary, we have presented a straightforward method to generate *local* pseudopotentials. These are capable of self-consistently describing

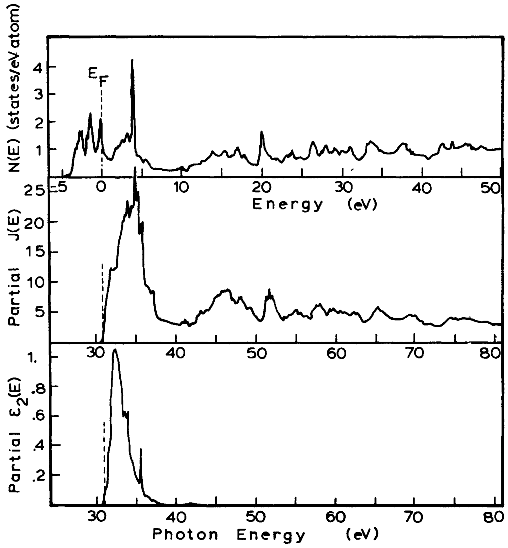

FIG. 3. Density of states $N(E)$ (top), partial joint density of states $J(E)$ (middle), and partial $\epsilon_2(E)$ (bottom). The partial $J(E)$ and $\epsilon_2(E)$ spectra are obtained from the 4*p* core band. Note the different energy scale for the top part of this figure.

the valence shell electrons of a neutral atom and its associated ionic configurations with very good accuracy. This is accomplished while using only two parameters. The applicability of the method to *d-band metals* has been demonstrated in the case of niobium. Without recourse to fitting any *crystalline* properties the self-consistent Nb *atomic* pseudopotential was successfully employed for the calculation of the crystalline electronic structure. We have found the resulting band structure and DOS to be in very good agreement with various first-principle calculations. Two regions of distinctly different electronic character in the density of states could be demonstrated. In addition, the $4p$ core band was used to predict the shape of absorption measurements into states up to 50 eV above E_F.

Though the range of possible applications of our approach may be limited by the cancellation rule[15,16] we believe that the first-principles-like nature of the generated pseudopotentials could be successfully employed in investigations of a wide variety of physical systems. It should also be noted that an interesting extension of our theory would be to do OPW-type calculations by orthogonalizing the basis set of plane waves to the pseudo core wave functions. This would constitute a considerable simplification to standard OPW calculations.

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