

field by surface charges. If the experimental results are interpreted in terms of surface effects, the broadening of the DTA signal towards lower temperatures indicates a lower disordering temperature of the dipoles in the surface region as compared to the dipoles in the interior. The number of dipoles in the surface region may be taken from the area under the broadened shoulder of the endothermal signal. Provided the latent heat of disordering is identical to that of the bulk, the fraction of "surface dipoles" is estimated to be about 30% to 50%. This value coincides with the number of NaNO_2 molecules located at the free surface of a 5-nm crystal. In other words, surface effects are restricted to about one monolayer. There is little evidence for the existence of "dead layers"² at the surface and for particle-size effects on the disordering of the "volume dipoles" as concluded from the unshifted peak temperature.

The interpretation of the experimental data by analogy to superparamagnetism appears unlikely as it requires the "surface" and "volume" dipoles

to disorder simultaneously. Simultaneous disorder of both types of dipoles implies an enhanced dipole coupling in the surface region⁴ which appears implausible in view of the reduced coordination number. In addition, it would be hard to understand in terms of this model why the DTA peak is broadened but not shifted.

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Efficacious Form for Model Pseudopotentials

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A simple way has been discovered to put model pseudopotentials, $V(\vec{r}) = \sum_{lm} |Y_{lm}\rangle V_l(r) \times \langle Y_{lm}|$, into a form which reduces the number of integrals of $V(\vec{r})$ required for an energy-band calculation from $mn(n+1)/2$ to mn for each l in the sum (where n is the number of plane waves used in the expansion and m the number of points in the Brillouin zone at which the calculation is performed). The new form may be chosen to improve the accuracy of the pseudopotential when used in other chemical environments.

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Pseudopotentials may be divided into three classes, of which one is empirical¹ and the other two are based on first principles. One of the first-principles pseudopotentials is obtained by adding some core functions ψ_c to the wave function ψ to obtain a smooth pseudo wave function,

$$|\varphi\rangle = |\psi\rangle + \sum_c \alpha_c |\psi_c\rangle, \quad (1)$$

and in its most general (non-Hermitian) form is [see Austin, Heine, and Sham² (AHS)]

$$V_{ps}^{\text{AHS}} = V + \sum_c |\psi_c\rangle \langle F_c|, \quad (2)$$

where $F_c(\vec{r})$ is an arbitrary function. By substituting Eq. (1) into the Schrödinger equation, the

relation

$$\alpha_c = \langle F_c | \varphi \rangle / (E - E_c) \quad (3)$$

is obtained. Zwicker³ has shown that in general the AHS pseudopotential is nonvariational, i.e., first-order errors in a trial pseudofunction φ_t cause first-order errors of either sign in the energy E_t . The original Phillips-Kleinman (PK) pseudopotential^{4,5}

$$V_{ps}^{\text{PK}} = V + \sum_c (E - E_c) |\psi_c\rangle \langle \psi_c| \quad (4)$$

has a nonunique φ because $\alpha_c^{\text{PK}} = \langle \psi_c | \varphi \rangle$ makes $\varphi' = \varphi + \sum_c \beta_c \psi_c$ a solution of Eq. (1). Zwicker³ was able to show that V_{ps}^{PK} is variational and

when used with a variational φ_t causes φ to become that unique φ which most closely approximates φ_t . Furthermore, it is obvious from

$$|\psi_t^{\text{PK}}\rangle = |\varphi_t\rangle - \sum_c \langle \psi_c | \varphi_t \rangle |\psi_c\rangle \quad (5)$$

that the trial PK wave function is always orthogonal to the core eigenfunctions. The AHS pseudopotential may also be made variational by making it Hermitian by setting $F_c = A_c \psi_c$, with A_c being a constant. In that case it is easy to see that ψ_t is not orthogonal to the ψ_c unless φ_t has sufficient variational freedom in the core region to make it so. Since the whole purpose of using a pseudopotential is to eliminate the need for core variational freedom in φ_t , we conclude that of this class of pseudopotentials, the PK form is the most efficacious. Pseudopotentials in this class have three shortcomings: (1) For valence functions which are orthogonal to all core functions such as oxygen $2p$ or iron $3d$, V_{Ps} reduces to V ; about this nothing can be done. (2) $V_{\text{Ps}}^{\text{PK}}$ depends explicitly on the eigenvalue E . This ultimately arises from the nonorthogonality of orthogonalized plane waves and causes no more trouble than the off-diagonal energy dependence of the secular equation obtained from any expansion in nonorthogonal basis functions. (3) Outside the core region the normalized φ is proportional to but not equal to ψ . Thus to perform an accurate self-consistent calculation, one must construct ψ using Eq. (1) or (5) and then renormalize it.

The "model" pseudopotential of Abarenkov and Heine⁶ is based upon the idea that the core is a black box from which the valence wave functions emanate with some logarithmic derivative and that any core pseudopotential which yields that logarithmic derivative is a valid first-principles pseudopotential. Thus the model pseudopotential may be written⁶

$$V_M = \begin{cases} V_{\text{val}}(\vec{r}) - \sum_{lm} |Y_{lm}\rangle A_l(E) \langle Y_{lm}| & \text{for } r < R_m, \\ -Z/r + V_{\text{val}}(\vec{r}) & \text{for } r > R_m, \end{cases} \quad (6)$$

where V_{val} is the Coulomb and exchange potential due to the valence electrons, Z is the valence

charge, and $A_l(E)$ is a constant (in space) function of E chosen to make the pseudofunction logarithmic derivative equal that of the true eigenfunction at several atomic eigenvalues. To a high degree of accuracy $A_l(E)$ may be linearized:

$$A_l(E) = A_l + B_l E. \quad (7)$$

This model pseudopotential contains two defects which in principle are irreparable although in practice are not too serious. Because the average potential in an infinite crystal is arbitrary, E in Eq. (6) is not uniquely determined when V_M is used in energy-band calculations. Note that this problem does not arise with $V_{\text{Ps}}^{\text{PK}}$ because $E - E_c$ is independent of a constant shift in the crystal potential. A second problem is the non-equality of the normalized pseudo wave functions and true wave functions for $r > R_m$. Because in this case the pseudofunction is not obtained from the wave function by the addition of core orbitals, there is no way to construct the wave function from a knowledge of the pseudofunction.

Recently a giant step forward in model pseudopotentials was taken by Hamann, Schlüter, and Chiang⁷ (HSC) who inverted the Schrödinger equation to obtain a model pseudopotential,

$$V_M^{\text{HSC}} = V_{\text{val}}(\vec{r}) + \sum_{lm} |Y_{lm}\rangle V_l^{\text{HSC}}(r) \langle Y_{lm}|, \quad (8)$$

where $V_M^{\text{HSC}}(r) \rightarrow -Z/r$ for $r > r_c$ (where r_c is a core cutoff radius). The real and pseudo wave functions of V_M^{HSC} are identical (not merely proportional) for $r > r_c$. Thus the need to calculate the true wave function is minimized.⁸ More importantly, it can be proven⁷ that as a consequence of the identity of the functions, the logarithmic derivatives and the first energy derivatives of the logarithmic derivatives of the true and pseudo wave functions are identical for $r > r_c$. Hence the energy dependence of V_M^{HSC} is second order and in most cases may be ignored. Kleinman⁹ has shown how $V_{l \pm 1/2}^{\text{HSC}}(r)$ may be obtained, which when used in the Schrödinger equation yields eigenvalues of the Dirac equation with $j = l \pm \frac{1}{2}$. Thus very accurate self-consistent relativistic energy-band calculations can be made with the following simple model pseudopotential used in the Schrödinger equation⁹:

$$V_M = V_{\text{val}}(\vec{r}) + \sum_{lm} |Y_{lm}\rangle [V_l^{\text{so}}(r) \vec{L} \cdot \vec{S} + \bar{V}_l^{\text{ion}}(r)] \langle Y_{lm}|, \quad (9)$$

where

$$V_l^{\text{so}} = \frac{2}{2l+1} [V_{l+1/2}^{\text{HSC}} - V_{l-1/2}^{\text{HSC}}], \quad (10)$$

$$\bar{V}_l^{\text{ion}} = \frac{1}{2l+1} [(l+1)V_{l+1/2}^{\text{HSC}} + lV_{l-1/2}^{\text{HSC}}]. \quad (11)$$

When attempting to use Eq. (9) for an energy-band calculation in which our basis functions were expanded in plane waves, we were thwarted by the huge number of integrals necessitated by the semilocal (i.e., nonlocal in angular coordinates but local in radial coordinate) part of the potential. Note that the integral of $|Y_{lm}\rangle V(r)\langle Y_{lm}|$ between a pair of plane waves is proportional to

$$\int j_l(kr)V(r)j_l(k'r)r^2 dr P_l(\cos\theta_{kk'}),$$

where the j_l are spherical Bessel functions and $P_l(\cos\theta_{kk'})$ is the Legendre polynomial of the angle between the wave vectors \vec{k} and \vec{k}' . If one has n different wave vectors at m points in the Brillouin zone, then for each l one has $mn(n+1)/2$ separate integrals to evaluate. In a thin-film calculation n can be as large as 1000 and m about 20, yielding 10^7 integrals. Note that this problem does not arise with the fully nonlocal pseudopotentials of the AHS or PK type. The integral of $|\psi_c\rangle\langle\psi_c|$, appearing in Eq. (4), between a pair of plane waves is proportional to

$$\int j_l(kr)\psi_c(r)r^2 dr \int j_l(k'r)\psi_c(r)r^2 dr P_l(\cos\theta_{kk'});$$

this factorization into a product of integrals involving only a single k requires the evaluation of only mn separate integrals for each ψ_c .

In order to circumvent this difficulty we first add and subtract a completely arbitrary function $V_L(r)$ from the relativistic form of Eq. (8) [or equivalently from Eq. (6)] to obtain

$$V_M^{j=l\pm 1/2} = V_{\text{val}}(\vec{r}) + V_L(r) + \sum_{lm} |Y_{lm}\rangle \delta V_{l\pm 1/2} \langle Y_{lm}|, \quad (12)$$

where $\delta V_{l\pm 1/2} = V_{l\pm 1/2}^{\text{HSC}}(r) - V_L(r)$. With $\Phi_{l\pm 1/2,m}(\vec{r}) = \varphi_{l\pm 1/2}(r)Y_{lm}(\theta, \varphi)$, we write down a nonlocal pseudopotential to replace the semilocal term, $V_{\text{SL}}^{j=l\pm 1/2}$, in Eq. (12):

$$V_{\text{NL}}^{j=l\pm 1/2}(r) = \sum_{lm} \frac{|\delta V_{l\pm 1/2}(\Phi^0)_{l\pm 1/2,m}\rangle \langle (\Phi^0)_{l\pm 1/2,m} \delta V_{l\pm 1/2}|}{\langle (\Phi^0)_{l\pm 1/2,m} | \delta V_{l\pm 1/2} | (\Phi^0)_{l\pm 1/2,m} \rangle}. \quad (13)$$

The superscript zero indicates that $(\Phi^0)_{l\pm 1/2,m}$ is the pseudo eigenfunction for which $V_{\text{SL}}^{j=l\pm 1/2}$ was calculated. Note that

$$V_{\text{NL}}^{j=l\pm 1/2} |(\Phi^0)_{l'\pm 1/2,m'}\rangle = |\delta V_{l'\pm 1/2}(\Phi^0)_{l'\pm 1/2,m'}\rangle$$

and that

$$V_{\text{SL}}^{j=l\pm 1/2} |(\Phi^0)_{l'\pm 1/2,m'}\rangle = |Y_{l'm'}\rangle \delta V_{l'\pm 1/2} |(\varphi^0)_{l'\pm 1/2}\rangle = |\delta V_{l'\pm 1/2}(\Phi^0)_{l'\pm 1/2,m'}\rangle$$

so that¹⁰

$$V_{\text{NL}}^{j=l\pm 1/2} |(\Phi^0)_{l'\pm 1/2,m'}\rangle = V_{\text{SL}}^{j=l\pm 1/2} |(\Phi^0)_{l'\pm 1/2,m'}\rangle. \quad (14)$$

TABLE I. Dirac-equation eigenvalues for W and two of its ions and the errors obtained by using the semilocal and nonlocal pseudopotentials. There are no errors in the W^+ pseudopotentials because they were constructed from that configuration. There are no bound $5f$ states in the $5d^46s^2$ configuration.

	W ($5d^46s^2$)			W ⁺ ($5d^46s^1$)		W ²⁺ ($5d^46s^0$)	
	Dirac (eV)	Δ (SL) (meV)	Δ (NL) (meV)	Dirac (eV)	Dirac (eV)	Δ (SL) (meV)	Δ (NL) (meV)
$6s_{1/2}$	-5.890	-13	-9	-12.509	-19.637	42	33
$6p_{1/2}$	-1.988	-5	-4	-7.710	-14.084	33	26
$6p_{3/2}$	-1.491	-4	-4	-6.897	-12.962	31	24
$5d_{3/2}$	-5.144	-14	-1	-12.415	-20.589	33	8
$5d_{5/2}$	-4.421	-15	-2	-11.644	-19.762	35	11
$5f_{5/2}$	-0.981	-4.404	11	12
$5f_{7/2}$	-0.981	-4.400	10	11

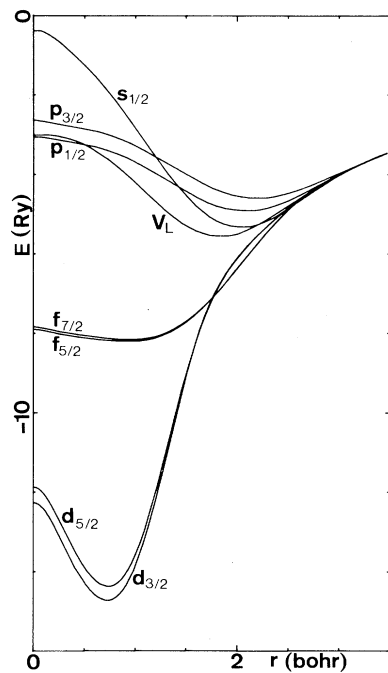


FIG. 1. The ionic pseudopotentials $V_{l\pm 1/2}^{\text{HSC}}(r)$ and $V_L(r)$ all of which approach $-2Z/r$ for large r .

By this trivial replacement of V_{SL} by the factorized V_{NL} we reduce the number of plane-wave integrals¹¹ required for each l from $mn(n+1)/2$ to mn . Note also that when the pseudopotential is transported to another atomic configuration or to a crystalline environment $(\Phi^0)_{l\pm 1/2, m'}$ is replaced by $\Phi_{l\pm 1/2, m'}$ and Eq. (14) does not hold. Because one has a great deal of freedom in choosing V_{NL} (due to the arbitrariness of V_L), the fact that $V_{\text{NL}}^{j=l\pm 1/2}|\Phi_{l\pm 1/2, m'}\rangle$ is not equal to $V_{\text{SL}}^{j=l\pm 1/2} \times |\Phi_{l\pm 1/2, m'}\rangle$ may be used to reduce the error incurred in transporting the pseudopotential.

We have constructed relativistic $6s$, $6p$, $5d$, and $5f$ pseudopotentials for singly ionized tungsten in the configuration¹² $5d^46s^1$. The Dirac eigenvalues listed in Table I were obtained with use of the Wigner interpolation formula for the correlation potential and the relativistic^{13,14} Kohn-Sham exchange potential. The pseudopotentials which are displayed in Fig. 1 were constructed with cutoff functions⁷ of the form $\exp[-(r/r_c)^{3.5}]$ with $r_c = 1.20, 1.75, 1.85,$ and 1.85 bohrs for the $5d$, $6s$, $6p$, and $5f$ potentials. V_L was taken to have the form (in rydbergs)

$$V_L = -\frac{2Z}{r} \left\{ 1 - \exp\left[-\left(\frac{r}{\alpha}\right)^{3.5}\right] + \gamma r \exp\left[-\left(\frac{r}{\beta}\right)^{3.5}\right] \right\}, \quad (15)$$

with $Z=6$, $\alpha=1.75$, $\beta=1.8$, and $\gamma=0.25$. Both V_{SL} and V_{NL} yield the same eigenvalues as the Dirac equation for this configuration. When transported to the $5d^46s^2$ atomic and $5d^46s^0$ doubly ionized configurations the eigenvalues of these pseudopotentials differ from the Dirac eigenvalues by the small amounts listed in Table I. The parameters in V_L have been chosen to make the V_{NL} eigenvalues more nearly correct than the V_{SL} . This particular choice of V_L makes V_{NL} worse with respect to V_{SL} when transported to configurations with a different number of d electrons. However, with a few more parameters we were able to construct a V_L which yielded a V_{NL} that was better than V_{SL} for both classes of configurations.

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¹¹If the integrals are to be calculated in real space, we have reduced some n^3 three-center integrals down to n^2 two-center integrals.

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