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Nonlinear ionic pseudopotentials in spin-density-functional calculations

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A new method for generating and using first-principles pseudopotentials is developed to treat explicitly the nonlinear exchange and correlation interaction between the core and the valence charge densities. Compared to existing potentials, the new scheme leads to significant improvement in the transferability of the potential. In particular, the spin-polarized configurations are well described with a single potential. The need for separate spin-up and spin-down ionic pesudopotentials is, thus, eliminated. The method can easily be implemented with minimal increase in computational effort. Results for both atoms and solids are demonstrated.

I. INTRODUCTION

In the past several years, the pseudopotential approach coupled with the density-functional scheme has had tremendous success in describing the electronic and structural properties of nonmagnetic systems.[1,2] In this paper, we propose a method which makes it possible to extend these calculations to magnetic systems. With a single spin-independent ionic potential, the method incorporates the local-spin-density approximation[3,4] to the exchange and correlation energy into the pseudopotential scheme. Problems such as those concerning properties of magnetic materials, spin-density waves, magnetic effects on surfaces, localized impurity states in defects, etc., can now be treated with the same ease and accuracy as in the nonmagnetic case. In addition the accuracy is in many cases improved even in the paramagnetic limit.

In an earlier scheme for introducing magnetic effects into pseudopotential calculations Zunger[5] proposed constructing separate ionic potentials for the spin-up and spin-down electrons. In this spin-dependent pseudopotential approach, the ionic pseudopotential in the solid depends on the spin density of the valence electrons, and it is obtained by interpolation between the ionic potential for the paramagnetic atom and that of the fully spin-polarized atom. We shall show that it is unnecessary and, in fact, often undesirable to employ these spin-dependent ionic pseudopotentials.

In the density-functional formalism,[6,7] the total energy of the ground state is given as a functional of the total electron charge density,

$$E_{\text{tot}}=T\{\rho\}+E_{\text{ion}}\{\rho\}+E_{ee}\{\rho\}+E_{\text{xc}}\{\rho\} \ , \quad (1)$$

where the various terms represent the kinetic energy, the electrostatic interaction of the ions with the electrons, the electrons with the electrons, and the exchange and correlation energy, respectively. The exchange and correlation energy is usually approximated by some local (nonlinear) function of the charge density, and the kinetic energy is found from the gradient of the now obtainable single-particle wave functions. Thus,

$$E_{\text{ion}}=\int V_{\text{ion}}(\vec{r})\rho(\vec{r})\,d^3r \ , \quad (2)$$

$$E_{ee}=\tfrac{1}{2}\int \frac{\rho(\vec{r}\,')\rho(\vec{r})}{|\vec{r}\,'-\vec{r}|}d^3r'd^3r \ , \quad (3)$$

$$E_{\text{xc}}=\int \epsilon_{\text{xc}}[\rho(\vec{r})]\rho(\vec{r})\,d^3r \ . \quad (4)$$

The charge density, in the pseudopotential formalism, is divided into core and valence contributions, and the energy of the core is assumed to be constant and subtracted out. Furthermore, the core contribution is often completely neglected, and the total energy is given by the above expressions with the total charge density replaced by a (pseudo) valence charge density, and V_{ion} replaced by the pseudopotential. All interaction between the core and valence electrons is thus transferred to the pseudopotential.[8] This implies a linearization of the interaction which can only be an approximation to the kinetic energy and the *explicitly* nonlinear exchange and correlation energy. If the core and the valence charge densities are well separated in space this will introduce no serious errors, as can be seen from the many successes of the method. However, if there is significant overlap between the two densities, the linearization, in particular of the exchange and correlation, will lead to reduced transferability of the pseudopotential and to systematic errors in the calculated total energy.

In the spin-density formalism the exchange and correlation energy depends on the local spin density as well as on the charge density. This additional spin dependence introduces additional nonlinearity, and it is the errors introduced by the linearization described above that have made it necessary to use spin-dependent ionic pseudopotentials. The scheme to be described, on the other hand, treats these nonlinear terms explicitly, and the need for separate spin-up and spin-down ionic pseudopotentials is thus eliminated. Moreover, the approach leads to significant improvement in the transferability of the potentials and therefore will yield more accurate results both for magnetic and nonmagnetic systems.

The remainder of the paper is organized as follows. In Sec. II the formulation for incorporating the nonlinear interaction of the core and valence densities into self-consistent pseudopotential calculations is presented. Section III describes the details of the calculation. Results obtained using local-density- and local-spin-density-functional calculations on both atoms and solids are discussed in Sec. IV. Finally in Sec. V a summary and some conclusions are given.

II. THEORY

Simple procedures[9–11] have been formulated to extract first-principles ionic pseudopotentials from atomic calculations. For example, in the norm-conserving pseudopotential scheme of Hamann, Schlüter, and Chiang[9] (HSC), angular-momentum-dependent screened atomic pseudopotential, V^l, are first constructed with the constraints that:

(1) The valence eigenvalues from the all-electron calculation and those from the pseudopotential calculation agree for a chosen prototype configuration.

(2) The all-electron wave functions and the pseudo-wave functions agree beyond a chosen core radius, r_c.

With these constraints, HSC showed that the potentials have two centrally desirable properties. The electrostatic potential produced outside r_c is identical for the all-electron and the pseudocharge distribution; the scattering properties of the all-electron atoms are reproduced with minimum error as the electronic eigenvalues move away from the prototype atomic levels. These two properties ensure a reasonable transferability of the pseudopotentials. The final bare-ion pseudopotentials, V^l_{ion}, are extracted from the neutral potentials by subtracting from each neutral V^l the Coulomb and exchange and correlation potentials due to the pseudovalence charge density, $\rho^v(r)$. For example, for a given angular momentum component l and spin component σ, the ionic potential is given by

$$V^{l\sigma}_{\text{ion}}(\vec{r})=V^{l\sigma}(\vec{r})-V_{ee}[\rho^v(\vec{r})] -V_{\text{xc}}[\rho^v(\vec{r}),\xi^v(\vec{r})]\ , \tag{5}$$

where

$$\xi^v(\vec{r})=\frac{\rho^v_+(\vec{r})-\rho^v_-(\vec{r})}{\rho^v(\vec{r})} \tag{6}$$

is the spin polarization of the valence charge with the + and − signs denoting the spin-up and spin-down electrons, respectively. Ionic potentials generated this way for the nonmagnetic case, i.e., $\xi=0$, have been shown to be highly accurate in many applications.[1,2] The basic assumptions in the above procedure are the frozen-core approximation and a decoupling of the core charge in the determination of the exchange and correlation potential seen by the valence electrons. The frozen-core assumption, however, implies a single ionic pseudopotential which is independent of the spin polarization of the valence states. It is the second approximation that gives rise to the spin-dependent ionic potentials in previous work. In the HSC approach, the total exchange and correlation potential is implicitly written as the identity

$$V^{\sigma}_{\text{xc}}(\rho^v+\rho^c,\xi)=[V^{\sigma}_{\text{xc}}(\rho^v+\rho^c,\xi)-V^{\sigma}_{\text{xc}}(\rho^v,\xi^v)] +V^{\sigma}_{\text{xc}}(\rho^v,\xi^v)\ , \tag{7}$$

where

$$\xi(r)=\frac{\rho^v_+(\vec{r})-\rho^v_-(\vec{r})}{\rho^v(\vec{r})+\rho^c(\vec{r})}\ . \tag{8}$$

Notice that ξ can be quite different from the valence polarization defined in Eq. (6). In the construction of the ionic potential, the terms in brackets are included in the ionic potential as part of the core properties. Since V_{xc} is a nonlinear function of the charge density,[3,4,12] the valence charge does not cancel, and the ionic pseudopotentials are dependent on the valence configuration. This feature is highly undesirable since it reduces the transferability of the potential. In particular, for magnetic applications, the spin-density distribution of the electrons can be extremely different both in magnitude and in profile as one goes from the atomic case to the various condensed-matter systems.[13] It is therefore unlikely that any interpolation formula between spin-up and spin-down potentials generated from atoms will work satisfactorially.

The dependence of the ionic pseudopotential on the valence charge apparent from Eq. (7) can be removed in a simple and straightforward way. We replace Eq. (5) by

$$V_{\mathrm{ion}}^{l\sigma}(\vec{r})=V^{l\sigma}(\vec{r})-V_{ee}(\rho^{v}(\vec{r}))-V_{\mathrm{xc}}^{\sigma}(\rho^{v}(\vec{r})+\rho^{c}(\vec{r}),\xi(\vec{r}))\ . \tag{9}$$

The total exchange and correlation potential, including the nonlinear core valence term, is now subtracted out of the neutral potential.[14] As we shall demonstrate in Sec. IV the result is an ionic potential highly transferable and essentially independent of the spin polarization and the prototype atomic configuration.

III. IMPLEMENTATION OF THE METHOD

In the employment of the new potential, the core charge must be added to the valence charge whenever the exchange and correlation potential or energy is computed. Within the rigid-core approximation, this core charge remains the same in all applications. Therefore, in addition to the usual *s*, *p*, and *d* potentials, we need to retain the core charge density which is computed once and for all in the same atomic calculations as the pseudopotentials.

In an atomic calculation there is, of course, no difficulty in representing the core charge. In a bulk calculation, however, there are two practical considerations that must be made. In any pseudopotential calculation there are small, but inevitable errors in the calculated valence charge density. Usually this leads to a negligible error in the total energy, but when the core charge is added, any inaccuracy in the valence charge density inside the core region is multiplied by the core charge and the error in the total energy will increase proportionally. To ensure the accuracy of the calculation, it is therefore very important to treat the effect of the core charge as a perturbation, and a change in the total energy as a result of this correction should be small. Second, for the implementation in plane-wave-expansion methods, we would like to represent all quantities in Fourier space. Although it does not enter the Hamiltonian matrix, the full core charge, with its very high Fourier components, is still impractical to use.

Fortunately both of the above concerns can be resolved by observing that the core charge has significant effect only where the core and the valence charge densities are of similar magnitude. It is without importance close to the nucleus where most of the core charge resides. We can therefore replace the full core charge density with a partial core charge density which is equal to the true charge density outside some radius r_0 and arbitrary inside. Tests show that r_0 may be chosen as the radius where the core charge density is from 1 to 2 times larger than the valence charge density. Inside r_0 we construct a partial core density equal to some function that matches onto the true charge density at r_0, is easy to Fourier transform, and gives the smallest possible integrated charge density. We have found that the spherical Bessel function j_0 best fulfills these criteria. Thus the core charge in Eqs. (8) and (9) is replaced by

$$\rho_{\mathrm{partial}}^{c}(r)=\begin{cases}A\sin(Br)/r & \text{if } r<r_0\\ \rho^{c}(r) & \text{if } r>r_0\end{cases} \tag{10}$$

where A and B are determined by the value and the gradient of the core charge density at r_0.

IV. NUMERICAL RESULTS

The new method has been tested for spin-polarized atomic silicon, molybdenum, and also for metallic sodium. For the atoms we have performed parallel all-electron and pseudoatom calculations using pseudopotentials with and without the core correction. In both cases the local-spin-density formulation of Gunnarson and Lundqvist[4] was used. The pseudopotentials were generated from the paramagnetic atoms using a suitably modified HSC scheme. The valence configurations were $3s^{1}3p^{3}$ for silicon and $4d^{5}5s^{1}$ for molybdenum. The potentials were then used to calculate the pseudoatoms in the configurations with the largest possible spin polarization. The resulting term values and the difference in the total energy between the paramagnetic and the spin-polarized atoms are given in Table I. We observe that the

TABLE I. Atomic term values and total energy differences between paramagnetic and fully spin-polarized atoms. Paramagnetic configurations are $3s^1 3p^3$ for Si and $4d^5 5s^1$ for Mo. All energies are in eV. ΔE is the total energy difference between the paramagnetic and the spin-polarized configuration. (Superscripts indicate the electron occupation and the $\pm$ signs denote the spin configuration for each orbital.)

			All electron	No core	Full core	Partial core
		$3s^1+$	−12.76	−12.82	−12.76	−12.76
	Term	$3p^3+$	−5.79	−5.81	−5.80	−5.80
	values	$3s^0-$	−7.55	−5.63	−7.56	−7.55
		$3p^0-$	−1.21	−0.43	−1.21	−1.20
Si						
	Total	ΔE	−3.58	−4.05	−3.61	−3.62
	energy	error		13.1%	0.7%	1.0%
		$4d^5+$	−5.24	−5.51	−5.24	−5.25
	Term	$5s^1+$	−4.79	−4.71	−4.81	−4.80
	values	$4d^0-$	−2.01		−2.00	−1.89
		$5s^0-$	−2.08	−1.02	−2.06	−2.05
Mo						
	Total	ΔE	−4.35	−8.46	−4.38	−4.52
	energy	error		94.6%	0.8%	3.9%

linear pseudopotential is marginal for spin-polarized silicon and inadequate for molybdenum. The core correction is capable in both cases of correcting the error, and the partial core does almost as well. We note that without the correction the unoccupied levels are too high in energy. In the case of silicon, this reverses the energy levels for the occupied p state and the unoccupied s state, making the fully spin-polarized atom seem stable. In molybdenum the improvement is even more striking. The uncorrected calculation overestimates the energy difference between the paramagnetic and spin-polarized configuration by almost a factor of 2. With the correction the error is reduced to an acceptable level.

The solid was tested by generating two pseudopotentials with different valence configurations. Here we used the formulation of Hedin and Lundqvist[15] for the exchange and correlation. These potentials were then used to calculate the static structural properties for sodium. For a perfectly transferable potential these properties should be independent of the configuration used for generation. The amount by which they change therefore measures the transferability. In Table II we give values for the calculated lattice constant and the bulk modulus. The first of the two potentials was generated with the highly ionic configuration $3s^{0.1}3p^{0.05}3d^{0.05}$, whereas for the second potential we used the neutral configuration $3s^{0.8}3p^{0.1}3d^{0.1}$. As could be expected, the pseudopotentials generated from the neutral configuration give the best results. The corrected potentials show excellent transferability but the uncorrected potential derived from the ionic atomic configuration fails miserably.[16]

The results that we obtain for the structural properties of sodium depend strongly on the choice of the exchange and correlation potential. The reason for this is probably related to the large

TABLE II. Lattice constants and bulk moduli for sodium in the body-centered-cubic structure calculated with and without the core correction for two different pseudopotentials. Potential 1 was generated with the ionic configuration $3s^{0.1}3p^{0.05}3d^{0.05}$ and potential 2 with the neutral configuration $3s^{0.8}3p^{0.1}3d^{0.1}$.

	Potential number	Lattice constant (Å)	Bulk modulus (10^{10} J m^{-3})
Without	1	3.58	1.63
core	2	4.02	0.97
correction	change	−11.0%	68.0%
With	1	4.03	0.95
partial core	2	4.09	0.95
correction	change	−1.3%	0.6%
All electron[a]		4.08	0.9

[a] Reference 17.

compressibiliy of sodium. The bulk modulus is less than one-tenth of that of aluminum. Small changes in the correlation energy can therefore have a large effect. For this reason we have chosen to compare with an all electron calculation[17] using the same type of correlation. The experimental values[18] $a=4.23$ Å and $B=0.68\times10^{10}$ J m^{-3} are somewhat different than the calculated numbers. We have also performed calculations using Wigner's interpolation formula for the correlation,[19] and we then obtain results in reasonable agreement with the experiment.

V. SUMMARY

We have shown that significant improvement in the transferability of pseudopotentials can be obtained by including a partial core charge in the treatment of the exchange and correlation. The increased transferability is of particular value in magnetic systems and has eliminated the need for special spin-polarized potentials. In some special cases, like the alkali metals, we find improvement even for nonmagnetic systems.

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