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Hartree-Fock core local-density-approximation valence pseudopotentials

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We derive the pseudopotential for an atom in which all the electrons are subject to a Hartree-Fock exchange potential arising from the core electrons, and a Kohn-Sham exchange-correlation potential arising from the valence electrons. When this ionic pseudopotential is transferred to a crystal, the self-consistent valence exchange-correlation potential has the simple form $V_{XC}^{val}=V_{XC}(\rho_{val})$. We show by explicit calculations of the lattice constants, cohesive energies, and bulk moduli of Na and GaAs that this pseudopotential is of similar quality, but has certain computational advantages over, a strictly local-density-approximation (LDA) pseudopotential with $V_{XC}^{val}=V_{XC}(\rho_{total})-V_{XC}(\rho_{core})$. It is far superior to the LDA pseudopotential with $V_{XC}^{val}=V_{XC}(\rho_{val})$.

In constructing norm-conserving ionic pseudopotentials[1] for use in condensed-matter calculations, one first constructs an atomic pseudopotential and then subtracts off the valence-electron contribution to that pseudopotential. It has long been known that because of its nonlinear dependence on charge density ρ, the local-density approximation (LDA) for the valence-electron exchange-correlation potential V_{XC}^{val} was not simply a function of ρ_{val}. However, to the extent that the atomic and condensed-matter valence charge densities were similar in the core region, it was assumed that the error in taking $V_{XC}^{val}=V_{XC}^{val}(\rho_{val})$ was small. Louie, Froyen, and Cohen[2] (LFC) showed, however, that an ionic pseudopotential obtained in this manner was highly nontransferable in two completely different cases: They showed that Si and Mo pseudopotentials obtained from paramagnetic valence configurations resulted in large total-energy errors when applied to spin-polarized configurations, and they showed that the lattice constant and bulk modulus of Na were vastly different for pseudopotentials obtained with two different atomic valence configurations. They showed that these transferability problems disappear when V_{XC}^{val} is taken to be $V_{XC}(\rho_{total})-V_{XC}(\rho_{core})$. This corresponds to using the full exchange-correlation (XC) potential and adding (to the ionic pseudopotential) and subtracting (from the self-consistent valence potential) the same function, and thus must remove all transferability problems associated with taking V_{XC}^{val} to be $V_{XC}^{val}(\rho_{val})$.

In performing *ab initio* molecular-dynamics calculations,[3] it becomes somewhat unwieldy to carry around all the core charge densities. Furthermore, these calculations use three-dimensional fast-Fourier-transform integrations over a rather coarse mesh, and, therefore, the inclusion of sharply peaked core and total charge-density functions might be expected to cause numerical errors (although this may be circumvented by using a partial core, as described in Ref. 2). We noted a recent calculation for liquid sodium in which an ordinary LDA pseudopotential was used; this pseudopotential was such that when it was used for solid Na, it resulted in an 11% error in the equilibrium lattice constant.[4] Thus, it occurred to us that a pseudopotential based on a Hartree-Fock (HF) atom would have a separable exchange potential and might be transferable to a crystal or liquid where the pseudopotential would represent a Hartree-Fock core, but where the valence electrons would be treated in the LDA. It then occurred to us, if we recalculated the atomic valence electrons by letting them (i) be subject to the Hartree-Fock potential from the previously calculated HF core functions (now taken to be rigid), and (ii) interact with each other via the LDA, their treatment would be closer to that in the solid or liquid; thus the pseudopotential obtained from the mixed HF-LDA atom would be more transferable thereto. Because of the nonlocal nature of the exchange operator, the Hartree-Fock core and valence functions are slightly admixed. This causes the HF potential resulting from the core functions to have an extremely long-range tail, which becomes very tedious if not impossible to treat correctly, especially when the Kleinman-Bylander[5] (KB) separable form of the pseudopotential is used. Therefore we finally chose to construct the pseudopotential from an atom in which all the electrons experience a Hartree-Fock potential arising from the core electrons and an LDA potential (exchange-plus-Wigner correlation) from the valence electrons. Shirley *et al.*[6] have constructed pseudopotentials from atoms in which a Hartree-Fock-exchange plus an LDA-correlation potential arises from all the electrons. It is well known[7] that the LDA overestimates correlation and underestimates exchange, so it makes sense to combine them; it is not so clear that a LDA correlation when added to a HF exchange is an improvement. In any event, the Shirley pseudopotential would be more appropriately used for dimers, where the same valence HF-exchange LDA-correlation potential can be used, than in condensed-matter calculations where an LDA exchange-correlation potential is used.

We compare with experiment the lattice constants, cohesive energies, and bulk moduli obtained for Na and GaAs using our HF-LDA pseudopotential and the LFC and ordinary pseudopotentials. We first calculated eigenvalues and eigenfunctions for the Dirac-LDA and Dirac-core HF, valence LDA atoms. We then used the Vanderbilt[8] procedure for constructing pseudopotentials that were as similar as possible (e.g., identical cutoff radii r_c) so that whatever differences we found could be attributed to how exchange and correlation were handled. If one is interested in the semilocal form of the pseudopotential, this is straightforward, but results in different (for different angular momenta) fairly long-range tails due to the core HF potential. A similar but local tail arises in the LFC ionic pseudopotential from the subtraction of $V_{\mathrm{XC}}(\rho_{\mathrm{core}})$ from $V_{\mathrm{XC}}(\rho_{\mathrm{total}})$. The nonlocal KB (Ref. 5) ionic pseudopotential is written as

$$V_{\mathrm{NL}}=V_L(r)+\sum_{l,m}\frac{|\delta v_l(r)\psi_{lm}(\mathbf{r})\rangle\langle\psi_{lm}(\mathbf{r})\delta v_l(r)|}{\langle\psi_{lm}|\delta v_l|\psi_{lm}\rangle}\ , \qquad (1)$$

where $V_L(r)$ is an arbitrary local pseudopotential, $\delta v_l(r)=V_l(r)-V_L(r)$ with $V_l(r)$ being the semilocal pseudopotential, and $\psi_{lm}(\mathbf{r})$ is the atomic eigenfunction of the V_l pseudopotential Hamiltonian.[9] For maximum transferability,[10] the $\delta v_l(r)$ should be as short range as possible, which means that $V_L(r)$ should be no longer range than $V_l(r)$. (By the range of V_l and V_L we mean the radius over which they differ from the real ionic potential; whereas, the range of δv_l is the radius over which it is nonzero.) Since the real ionic potential is l dependent (due to the HF core) over a greater range than V_l ordinarily would be, this presents a small problem. One way to handle it (hereafter referred to as HF-LDA) is to construct an atomic potential

$$v=V_{\mathrm{Coul}}+V_{\mathrm{XC}}(\rho_{\mathrm{val}})+f^{x}_{\mathrm{core}}\ , \qquad (2)$$

where f^{x}_{core} is any local core exchange. It could be taken to be an average of the l-dependent HF core exchange potentials, but we chose $f^{x}_{\mathrm{core}}=[V_x(\rho_{\mathrm{total}})-V_x(\rho_{\mathrm{val}})]_{\mathrm{LDA}}$ because the latter is of shorter range. Then v is pseudized in the standard manner,[8] but using the Dirac-HF-core, LDA-valence eigenfunctions and eigenvalues. Since this semilocal pseudopotential V_l is based on the local atomic potential v, the construction of V_{NL} proceeds as usual. Another choice (hereafter HF-LDA*) is to accept the long-range l dependence of V_l and choose V_L to become equal to the Coulomb potential beyond some radius, so that the tails on the δv_l arise from HF core exchange only, and thus may be invested with some physical significance.

We have performed the calculations for Na listed in Table I. In all cases except one, the Vanderbilt cutoff radii are $r_s=r_p=1.7$ bohrs, and in all cases except one, the plane-wave kinetic-energy cutoff was 15.174 Ry when $a=7.984$ bohrs with the same number of plane waves used for all a. This results in between 240 and 259 plane waves at the 40 special **k** points[11] sampled in the irreducible wedge of the Brillouin zone (BZ). The HF-LDA ionic pseudopotentials are displayed in Fig. 1. V_L is shown as a dashed line that follows V_p until just before it crosses V_s, and then it joins smoothly with V_s. A similar V_L was chosen for the LDA and LFC pseudopotentials. This insures that the δv_l do not change sign, and thus prevents the denominator in Eq. (1) from becoming small relative to the numerator, which can cause reduced transferability[10] and even "ghost" states[12] in extreme cases. In the HF-LDA* case, V_L starts out identically, but well past the minimum in V_s it joins smoothly to the ionic Coulomb potential (which is almost $2/r$ at that point.)

TABLE I. Comparison with experiment of Na lattice constant, cohesive energy, and bulk modulus calculated with several pseudopotentials.

	a (bohrs)	E_{coh} (eV)	B (10^{10} ergs cm^{-3})
Expt.	7.984	1.113	6.8
[HF-LDA ($3s^1$)]	8.235	1.0785	6.78
HF-LDA ($3s^1$)	8.233	1.0781	6.80
HF-LDA ($3s^{1/2}$)	8.232	1.0801	6.80
HF-LDA* ($3s^1$)	8.241	1.0757	6.82
HF-LDA* ($3s^{1/2}$)	8.241	1.0770	6.83
LFC ($3s^1$)	7.785	1.1342	8.00
LFC ($3s^{1/2}$)	7.780	1.1388	7.99
LDA ($3s^1$)	7.672	1.1538	8.33
LDA ($3s^{1/2}$)	7.543	1.1954	8.10
HF-LDA ($3s^1$)r_c	8.233	1.0766	6.78
HF-LDA ($3s^1$)L^a	8.263	1.0692	6.93
HF-LDA ($3s^1$)L^p	8.208	1.0930	6.98

The experimental values listed in the first row of Table I are taken from Kittel.[13] The lattice constant and cohesive energy are low-temperature results, whereas the bulk modulus is room temperature. There are two sets of low-temperature elastic constants listed by Huntington[14] that result in bulk moduli on either side of that in our table. The second row lists a fully converged calculation with a kinetic-energy cutoff of 60.696 Ry. Comparison with the third row shows that the 15.174-Ry-cutoff calculations are essentially converged. Comparison of rows 3–10 shows that the HF-LDA, HF-LDA*, and LFC pseudopotentials are highly transferable in the sense that the results obtained are almost independent of whether the pseudopotential is obtained from a $3s^1$ or a $3s^{1/2}$

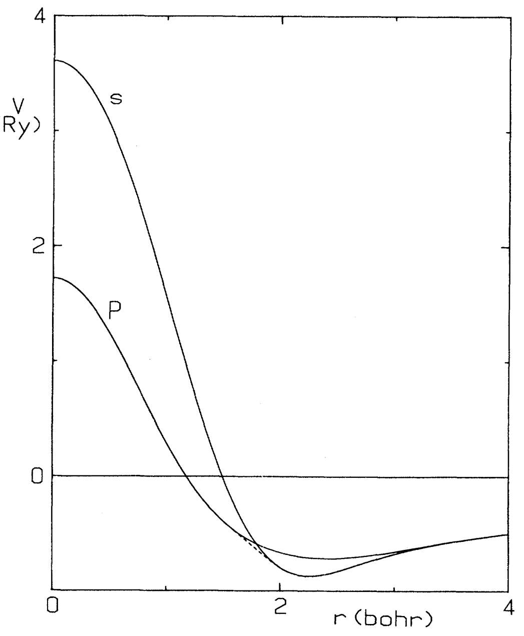

FIG. 1. The s and p HF-LDA pseudopotentials of Na. The local pseudopotential was chosen to lie along the dashed line connecting the s and p pseudopotentials.

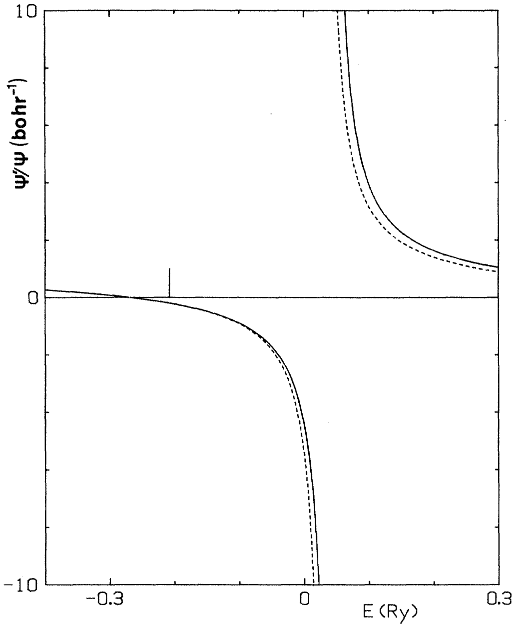

FIG. 2. Na logarithmic derivatives evaluated at $r=5$ bohrs. The all-electron Dirac atom and the HF-LDA ($3s^1$) pseudopotential results are indistinguishable and are represented by the solid curve. The HF-LDA ($3s^1$)L^p logarithmic derivative is the dashed curve. The marker on the energy axis is at the $3s$ eigenvalue.

atomic configuration; whereas, the LDA pseudopotential is not transferable. It is perhaps surprising that the HF-LDA and HF-LDA* are even more transferable than the LFC, since they use the same $V_{\rm XC}^{\rm val}=V_{\rm XC}(\rho_{\rm val})$ that the LDA does. We had been under the impression that the LFC pseudopotential worked so well because it makes the exchange potential insensitive to the valence charge density in the core region,[15] but that is obviously not the case. The HF-LDA, HF-LDA*, and LFC methods seem to be transferable because they handle exchange in correct, although different, ways. The last three rows of Table I demonstrate how calculated results depend on details of the construction of the pseudopotential. HF-LDA ($3s^1$)r_c is identical to HF-LDA ($3s^1$) except that the cutoff radii r_s and r_p are reduced to 1.5 bohrs. A part of the small reduction in cohesive energy is due to the shorter-range pseudopotential containing higher Fourier components, and hence being not quite so converged with the 15.174-Ry plane-wave cutoff. HF-LDA ($3s^1$)L^a is identical to HF-LDA ($3s^1$) except that V_L was constructed by joining V_s to V_p from above rather than below as in Fig. 1. This results in vastly changed δv_l (although they still have the desirable property of being of constant sign) and hence makes a small but non-negligible change in the calculated results. In HF-LDA ($3s^1$)L^p, $V_L=V_p$. This is convenient for large-scale computations since it makes $\delta v_p=0$. The ratio of the δv_s denominator in Eq. (1) to the same integral with δv_s replaced by its absolute value is[16] -0.159, which can be extremely dangerous.[10,12] In Fig. 2, we compare the all-electron, HF-LDA ($3s^1$), and HF-LDA ($3s^1$)L^p s logarithmic derivatives evaluated at $r=5$ bohrs as functions of energy. The HF-LDA ($3s^1$) curve is indistinguishable from the all-electron curve; whereas, the HF-LDA ($3s^1$)L^p curve differs from the other two by a significant amount. Nevertheless, the HF-LDA ($3s^1$)L^p pseudopotential yields a lattice constant and cohesive energy in better agreement with experiment than the HF-LDA ($3s^1$); we attribute this to a cancellation of errors inherent in the LDA by those introduced by the incorrect logarithmic derivative.

TABLE II. Comparison with experiment of GaAs lattice constant, cohesive energy per atom, and bulk modulus calculated with several pseudopotentials.

	a (bohrs)	$E_{\rm coh}$ (eV)	B (10^{11} ergs cm^{-3})
Expt.	10.683	3.35	7.55
HF-LDA	10.688	3.886	7.47
LFC	10.597	4.047	6.94
LFC(PC)	10.604	4.031	6.89
LDA	10.393	4.046	6.36
[HF-LDA]	10.754	3.945	6.98

The 3.1% discrepancy between our HF-LDA lattice constant and experiment, while smaller than the LDA discrepancy, is much larger than we are used to. We attribute this to the extreme softness of the Na lattice, which magnifies errors. We therefore compare the various pseudopotential results with experiment[17] for GaAs in Table II. The As atomic configuration is $4s^{1.75}4p_{1/2}^{0.917}4p_{3/2}^{1.833}$ and the pseudopotential cutoff radii $r_s=r_p=r_d=1.3$ bohrs; the Ga configuration is $4s^{1.75}4p_{1/2}^{0.25}4p_{3/2}^{0.50}$ and $r_s=r_p=r_d=1.5$ bohrs in all cases. The V_L for both Ga and As run from V_d to V_s and is always below V_p. The kinetic-energy cutoff is 16.9154 Ry at $a=10.683$ bohrs, which gives 344–361 plane waves at the 10 special **k**-point samples[11] of the BZ irreducible wedge. This cutoff, although as large as possible for large-scale calculations,[18] does not quite give convergence as the results in the last row, obtained with a 67.6616-Ry cutoff, demonstrate. In any event, the converged [HF-LDA] lattice constant has only a 0.66% discrepancy with experiment and the unconverged HF-LDA is in near perfect agreement. The HF-LDA bulk modulus and cohesive energy are in better agreement with experiment than the LFC, although had we calculated a fully converged LFC lattice constant, it would have been in better agreement with experiment than [HF-LDA]. [The LFC(PC) calculations use a partial core as described in Ref. 2.] And, as usual, the LDA results are the poorest.

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[15] Although the pseudocharge density is small in the core region, the cube root is a great multiplier and $V_x^{\text{val}}=V_x(\rho_{\text{val}})\sim\rho_{\text{val}}^{1/3}$ is large and sensitive to ρ_{val}. On the other hand, $V_x^{\text{val}}=V_x(\rho_{\text{total}})-V_x(\rho_{\text{core}})\sim(\rho_{\text{core}}+\rho_{\text{val}})^{1/3}-\rho_{\text{core}}^{1/3}\approx\frac{1}{3}\rho_{\text{val}}/\rho_{\text{core}}^{2/3}$ is negligible in the core region.

[16] The minus sign indicates that the large r part of V_s-V_p dominates the small r part in the integration.

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