

## Role of forms of exchange and correlation used in generating pseudopotentials

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We generate pseudopotentials using various treatments of exchange and correlation and test the pseudopotentials both for physical predictions that they make (with quantum Monte Carlo many-body calculations for the valence electrons) and for transferability. The calculated results for physical quantities (e.g., binding energies, ionization potentials, molecular dissociative energies, and bond lengths) are compared with each other and experiment for monatomic sodium, potassium, calcium, scandium, titanium, and silicon, and for diatomic sodium, potassium, and silicon. We find that pseudopotentials generated using Hartree-Fock exchange in conjunction with local-density correlation are more transferable and yield better physical ionic properties than those generated using either local-density exchange-correlation or pure Hartree-Fock exchange. For critical atoms like chromium and nickel we attribute the better transferability to the absence of the nonlinearity problem associated with local exchange. In particular, we find marked improvement in the  $3d$  energies for calcium, scandium, and titanium. Systematically obtaining better pseudopotentials may require a many-body treatment of correlation effects in the full-atomic configurations from which the pseudopotentials are generated.

### INTRODUCTION

The use of norm-conserving pseudopotentials<sup>1-4</sup> to describe valence properties of atoms (while removing core levels) is a well-established approach in conjunction with single-body methods.<sup>5</sup> Recently pseudopotentials have also been utilized in conjunction with methods which solve the full many-body problem of the interacting valence electrons, e.g., using the  $GW$  approximation of Hedin<sup>6</sup> for real systems,<sup>7</sup> as well as variational<sup>8</sup> and diffusion Monte Carlo.<sup>9</sup> Since the pseudopotentials used in these calculations are currently generated using single-body methods, a key question is the extent to which the initial approximate treatment of many-body effects (in particular dealing with exchange and correlation between core and valence electrons) is sufficiently accurate to warrant the use of these pseudopotentials in subsequent many-body valence-electron calculations.<sup>7,9</sup>

To address this question, we have conducted tests of pseudopotentials generated using several different single-body techniques, comparing with experimental values the predictions by the pseudopotentials of different physical quantities (ionization potentials, electron affinities, and various interconfiguration energies, as well as dimer properties) for various elements. For most elements we

studied, we were able to carry out quantum Monte Carlo many-body valence calculations to determine such quantities; this provided an absolute test for comparing the results of different pseudopotentials with experiment. Regarding single-body approximations used in treating exchange effects, we shall present a twofold argument for preferring Hartree-Fock exchange over local-density exchange.<sup>10</sup> However, none of the single-body treatments of correlation effects that we tested consistently led to results in good agreement with experiment, and we cannot recommend which form to use for correlation. Indeed, pseudopotentials which predict physical quantities consistently in good agreement with experiment may ultimately require using a more involved many-body method to compute the full-atomic configurations from which pseudopotentials are generated.

We have divided the body of this paper into two sections. In the first, we provide a background on pseudopotentials and various single-body techniques available for use in generating them. In the second, we describe the methods used to test the pseudopotentials, and we present the results of the tests. We then make some brief conclusions based on both the background material which we present and our own findings.

## BACKGROUND

Pseudopotentials can considerably simplify calculations of electronic structure. Here, we define pseudopotentials as artificial electron-ion interactions represented by nonlocal potentials which equal the full-atomic potentials outside of the atomic core.<sup>1-4</sup> They are usually constructed to self-consistently bind nodeless valence (pseudo-) wave functions with eigenvalues equal or close to the full-atomic valence eigenvalues, and have the full-atomic single-body scattering properties (partial-wave phase shifts or radial logarithmic derivative) for angular momenta of interest over a reasonably large energy range. By implementing a pseudopotential, one can systematically remove from a problem deep atomic core levels and the potentials which bind them. This is advantageous for a variety of reasons. The total number of electrons dealt with in a problem is reduced, which reduces the size of subsequent calculations. By eliminating tightly bound core levels and removing the oscillations from valence orbitals, orbitals may be represented by a variety of simple and/or small basis sets, and the spatial resolution needed to describe potentials and orbitals and the overall energy scale (time resolution) in a given problem are greatly reduced. Such simplifications are of paramount importance for many-body calculations employing both analytic and stochastic techniques.<sup>7-9,11</sup>

The pseudopotential calculation of the release-node diffusion Monte Carlo binding curve for, say, Si<sub>2</sub> (an eight-electron problem, once one is working with pseudopotentials rather than full-atomic potentials) required a few hours on a Cray Research, Inc., X-MP/48 supercomputer. This demonstrates the advantage of using pseudopotentials for simulating many-atom systems, since a Monte Carlo calculation even of one full-core silicon atom would clearly be a much more substantial calculation (by a factor of  $\sim 10^4$  to achieve the same accuracy of 0.1 eV), because of the overall energy, time-scale, and spatial-scale differences, in addition to having a larger number of electrons.

Using pseudopotentials to mimic an element's full-atomic valence properties—let us briefly set aside the question of whether the single-body technique (e.g., Hartree-Fock) used to determine such valence properties is sufficiently accurate—has rigorous physical grounds.<sup>4</sup> Most important, the disparity between the energy scales of core and valence electrons tends to decouple core shells from valence properties. This enables the pseudopotentials to mimic the valence properties of their full-atomic counterparts in various physical environments, i.e., to be “transferable.” Moreover, since the total energy is stationary with respect to electron wave functions, holding core orbitals fixed when changing the valence configuration of an atom (the “frozen-core” approximation) leads only to variational (second-order) total-energy errors.<sup>12</sup> Numerical tests by von Barth and Gelatt<sup>12</sup> and ourselves (unpublished) demonstrate that even the non-variational errors in single-particle valence eigenvalues tend to be small. All of these factors allow core orbitals to be approximated as producing a background potential

experienced by the valence orbitals, which, being nearly independent of the valence configuration, can in turn be replaced by a pseudopotential. “Norm-conserving”<sup>1,2,4</sup> or “shape-consistent”<sup>3</sup> pseudopotentials, which are the types of pseudopotentials generally used, obey a sum rule (norm conservation) which insures that the pseudopotential produces the full-atomic single-body scattering properties not only at the one energy where the pseudopotential reproduces the full-core atom by construction (the “reference valence configuration”), but over a range of energies.<sup>4</sup>

Shirley *et al.*<sup>4</sup> showed that it is possible in some cases to extend this energy range in the hope of reducing errors in the single-body properties of a pseudopotential. However, only when electrons are excited far (say, more than 10 eV) above the energy at which the pseudopotential has been generated will extension of norm conservation affect single-particle energies by more than a few hundredths of an electron volt. This is much smaller than the effects on single-particle energies present in pseudopotentials because they are generated using various single-body methods, and comparable to frozen-core and other pseudopotential errors. We therefore believe that the dominant factor determining differences between predicted and observed values of physical quantities of atomic and diatomic systems can be attributed to the single-body method used when one generates the pseudopotential, while additional errors inherent in the pseudopotential method itself may affect results by up to a tenth of an electron volt. The only exception to this is for transition-metal elements, where transferability errors can be several tenths of an electron volt.

Now, let us consider the consequences of using a single-body approximation to determine the valence properties of an atom which will be built into pseudopotentials. In general, whatever approximation of many-body effects is used, any errors in the pseudopotential will persist in the calculated valence properties unless they are artificially removed. For example, suppose one generates a pseudopotential for an atom or ion which has only one electron in the valence shell. If the pseudopotential faithfully represents the physical ion, the absolute value of the eigenvalue of the lowest-bound one-electron level should equal the experimental removal energy for each angular momentum of interest.<sup>13</sup> If it does not, there is a permanent error built into the pseudopotential. Ideally, one would solve accurately the many-body Schrödinger equation for the full atom and from the solution thereof obtain the single-body valence properties of the atom, making a pseudopotential to imitate those properties. An “exact” pseudopotential for atoms or ions with one valence electron could thus be produced; an exact pseudopotential with more than one electron in the valence shell would require more effort.

The full many-body Schrödinger equation for an assembly of electrons is

$$(T + U + V)\Psi(1, 2, 3, \dots, N) = E\Psi(1, 2, 3, \dots, N) . \quad (1)$$

$T$  is the kinetic-energy operator,  $U$  is the background

single-body potential in which the electrons move, and  $V$  is the two-body Coulomb interaction. The indices  $1, 2, 3, \dots, N$  denote the space and spin coordinates of the  $N$  electrons. The physical effects involved in the solution to this Schrödinger equation can be categorized into three groups of increasing difficulty: (a) Single-body motion, involving  $T, U$  and the direct Coulomb contribution from the average single-body charge density through  $V$ , (b) effects on single-body motion due to the nonlocal exchange Coulomb contribution from the average nonlocal single-body charge density through  $V$ , and (c) modifications to the above effects due to electron-electron correlations.

We are not aware of anyone having yet generated pseudopotential by a full, *ab initio* many-body calculation. Instead, there is a variety of single-body schemes used to solve only approximately the many-body problem. The Hartree-Fock (HF) approximation assumes a determinantal form of the many-body wave function, and addresses (a) and (b) directly but omits (c) altogether. The Hohenberg-Kohn-Sham local-density approximation<sup>10</sup> (LDA) treats (a) as in HF but avoids the difficulty of nonlocal potentials arising from (b) by including exchange effects only approximately, though the LDA also provides an equally simple but approximate form for (c). Since (b) and (c) are dealt with using only the local single-particle density, they are therefore treated exactly only in uniform systems, where exchange and correlation effects are known. The LDAX scheme, which was first proposed by Kohn and Sham<sup>10</sup> and has been implemented by many,<sup>14-16</sup> treats (a) and (b) in the direct fashion of HF, but (c) in the fashion of the LDA.

Unlike in HF, where the direct and exchange Coulomb interactions between an electron and itself cancel exactly, the exchange form used in the LDA only partially cancels the direct Coulomb self-interactions. In addition, LDA correlation contains spurious terms because an electron experiences an unphysical self-correlation potential that cancels part of its direct Coulomb self-interaction. Because of this, a number of self-interaction corrections (SIC's) have been developed to cancel the various unphysical self-interactions present in the LDA (Coulomb, exchange, and correlation) and LDAX (correlation only). Perdew and Zunger present one particular form of orbital-dependent SIC and refer to several other SIC schemes.<sup>17</sup> Stoll *et al.*<sup>16</sup> proposed an orbital-independent SIC for correlation only (to be used with Hartree-Fock exchange) which does better than the correlation only SIC of Perdew and Zunger in some situations, but not all.<sup>16</sup> We note that SIC's should be less important in LDAX, since then one only needs to deal with spurious self-correlation terms.

For the generation of pseudopotentials, the single-body methods commonly used in the full-atomic calculations have been the LDA and HF. We are not aware of previous attempts to include the LDAX and/or LDAX-SIC approaches in the generation of pseudopotentials.<sup>18</sup> Woodward and Kunz<sup>19</sup> have found that for atoms with  $Z < 21$ , there is little difference between HF's and the LDA's effects on valence properties. For the elements with  $Z < 21$  which we examined (sodium, silicon, potassi-

um, and calcium), we found large differences between LDA and HF pseudopotentials only for the  $3d$  level in calcium ( $Z=20$ ), which the LDA was significantly overbinding, and HF was significantly underbinding. We also found large differences from transition elements of larger atomic number, especially with regard to the  $d$  levels, while  $s$  and  $p$  states (and hence the properties of  $s$ - $p$  bonded systems) appear not to be as strongly affected for all the elements which we tested. For the remainder of this section, we shall mention some differences between results obtained using the LDA and HF methods to describe exchange and/or correlation effects, focusing on the effects that such differences have on pseudopotentials generated.

Regarding exchange effects, the form of exchange used in calculations affects the theoretical valence properties of transition-metals ions strongly. From full-atomic calculations (like those used in generating pseudopotentials) Gunnarsson and Jones<sup>20</sup> and Baroni and Tuncel<sup>14</sup> have noted that the angular character of  $d$  orbitals affects the degree to which they feel exchange effects at the same point in space compared to, say  $s$  orbitals, causing the  $d$  levels to be overbound when one uses LDA exchange.<sup>21</sup> If LDA exchange is used in generating pseudopotentials, then some information about nonlocal core-valence exchange will be lost, and this may be disadvantageous when such exchange is important. [Despite this, the LDA and particularly LDA-SIC often yield "good" numbers (numbers in good agreement with experiment) for total energy differences between two atomic configurations, because errors due to LDA exchange are partially cancelled by errors due to LDA correlation.<sup>21</sup>] Exchange splittings between majority spin and minority spin levels in a partially filled valence shell also depend on whether one uses HF or LDA exchange. Such splittings are generally underestimated by LDA exchange,<sup>20</sup> while HF tends to overestimate such splittings, which is attributed to its omission of screening effects. Since most screening of exchange is actually done by valence electrons,<sup>21</sup> however, and because of the above-mentioned disadvantages of LDA exchange, we believe it is appropriate to use unscreened HF exchange in generating pseudopotentials, provided screening of exchange among valence electrons is incorporated in subsequent many-body calculations.

To all of this we should add that transferability of pseudopotentials with LDA exchange requires corrections due to the nonlinearity of LDA exchange in the single-particle density and spin polarization,<sup>2,22</sup> while HF exchange is linear in the (nonlocal) two-body density matrix from which it is determined and therefore needs no such corrections. This is because HF relates the total energy of a system to the two-particle density, taking contributions from each pair of electrons and their single-particle densities separately, while the LDA relates the total energy to the total single-particle density, which is generally a nonlinear relationship.<sup>10</sup> Since the required corrections are large in some cases, this is a distinct advantage of using HF exchange in generating pseudopotentials. [We should meanwhile note that a HF exchange pseudopotential has the shortcoming that the nonlocal core-valence exchange potential as experienced by

valence electrons is usually frozen into a radially local potential representative only of the configuration in which the pseudopotential is generated, while in fact it depends on the valence configuration. This could potentially undermine the transferability of HF exchange pseudopotentials when core and valence orbitals overlap significantly,<sup>3</sup> though we have found that this error is quantitatively much smaller than the one induced by the nonlinear density dependence of local-density exchange potentials. The reason is probably that the main effect of nonlocality in the core-valence exchange potential is its different action on valence states of different angular momentum, which is preserved by the angular momentum dependence of the pseudopotential.<sup>23</sup> The radial nonlocality, which is actually lost by the HF pseudopotential, can cause serious transferability problems only when the radial valence orbitals are altered by more than a constant factor inside the core; such a shape distortion is usually of little effect and much smaller than the corresponding change in the density (which spoils the LDA pseudopotentials in case of significant core-valence overlap) for typical valence excitations.] Complications due to the nonlinearity of LDA exchange can be handled in the framework of pseudopotentials by adding terms to the Hamiltonian.<sup>2,22</sup> A novel, efficient scheme for implementing such corrections is to be presented in a future work.<sup>24</sup>

Regarding correlation effects, HF omits them altogether, and tends to underbind atoms and valence levels, i.e., both the total energy and the valence level eigenvalues are not sufficiently negative. On the other hand, LDA correlation tends to overestimate correlation contributions to the total energy of atoms.<sup>25</sup> This is in part due to the inclusion of self-correlation effects (particularly for the highly localized deep core levels) though LDA-SIC correlation used in conjunction with HF exchange gives very good total energies for atoms.<sup>14-16</sup> Proponents of the LDA (Ref. 10) have been careful to distinguish between its ability to estimate the exchange and/or correlation effects on the total energy of a system of electrons (which the LDA was formulated to compute) versus exchange and/or correlation effects on the single-particle eigenvalues. Thus, the effect of LDA or LDA-SIC correlation on pseudopotentials (which are fitted to match eigenvalues) is of crucial importance and should be examined. This is especially true in the present work since LDA correlation has usually been used in conjunction with LDA exchange by others, so that it was difficult to separately identify errors in the treatment of exchange and correlations which are built into pseudopotentials. Meanwhile, we should mention that there has also been work using limited configuration interaction techniques to estimate the correlation effects on valence properties of atoms due to the outermost core shell,<sup>26</sup> and in addition some workers have empirically adjusted HF pseudopotentials so that physical predictions by such pseudopotentials match experimental observation.<sup>27</sup> Basically, however, no single method has been presented which leads to pseudopotentials with the correct correlation effects built in for every element, and even the empirical corrections have been done only for systems with one electron outside of the core.

## GENERATING AND TESTING PSEUDOPOTENTIALS

### Methods

Self-consistent full-atomic calculations, including those used in generating pseudopotentials, were carried out for electrons obeying the Koelling-Harmon<sup>28</sup> scalar-relativistic Schrödinger equation on a radial mesh. This equation contains all features of the Dirac equation but averages over spin-orbit effects. Either HF or local-density exchange was implemented, depending on the form to be tested. When included, correlation effects were implemented via the spin-density generalization of the LDA as prescribed by Gunnarsson and Lundqvist,<sup>10</sup> using the parametrization of Perdew and Zunger<sup>17</sup> of the Ceperley-Alder correlation function.<sup>29</sup> We used the method of Perdew and Zunger for interpolating between the paramagnetic and spin-polarized formulas for correlation effects. When we examined the effects of including a SIC, we used that of Perdew and Zunger in conjunction with Krieger and Li's orbital-independent weighted average potential<sup>30</sup> (WAP) or the SIC by Stoll *et al.*

Norm-conserving pseudopotentials were obtained using Vanderbilt's method,<sup>31</sup> with one modification for the  $l=1$  pseudopotentials in sodium and potassium. For those we changed the parameter  $a$  in his cutoff function used in generating the pseudopotentials ( $x$  is the ratio of  $r$  to the cutoff radius),

$$h(x) = 100^{-\sinh^2(x/a)/\sinh^2(1)}. \quad (2)$$

This was done to have the pseudopotentials converged to full-atomic potentials well inside the bond midpoint of the alkali dimers we wished to study, yet not cause the pseudopotentials to become too hard. For these pseudopotentials, we decreased  $a$  in the potassium  $l=1$  channel from 1.5 to 1.3 and chose a core radius smaller than would usually be done because of the proximity of the last node in the valence atomic  $p$  wave functions to the dimer bond midpoint. [While the above cutoff function only deals with the product of  $a$  and the cutoff radius, Vanderbilt's method to generate pseudopotentials also includes a step which depends only on the cutoff radius. Thus, changing  $a$  and changing the cutoff radius does not produce the same results in the Vanderbilt approach. We refer the reader to his paper for details on the role of the cutoff radius and  $a$  (1.5 in his paper).] To push the node even closer to the nucleus we generated pseudopotentials for the  $l=1$  channels at +0.3 hartree in sodium and +0.5 hartree in potassium using Hamann's method.<sup>32</sup> The result was that the pseudopotentials all became equal to the full-atomic potential well within the dimer bond midpoint, while norm conservation was quite easily achieved using the small cutoff radius. This scheme lowered the bound  $p$  levels by some hundredths of an electron volt, but appears to have had no other physical effects, since results for our HF pseudopotentials agreed closely with those for HF pseudopotentials generated by other workers.<sup>27</sup>

We tested all of our pseudopotentials for transferability by evaluating interconfigurational changes in total energy given by full-atom and pseudopotential calculations, ex-

aming the nonsphericalized total energy given the radial wave functions derived from our spherical atomic program. This included spin-orbit splittings via first-order perturbation theory, where such a spin-orbit Hamiltonian written in hartree atomic units is

$$\mathcal{H}_{s.o.} = \sum_{i=1}^N \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{\partial V}{\partial r_i} \mathbf{l}_i \cdot \mathbf{s}_i . \quad (3)$$

This is a proper accounting for spin-orbit splittings when exchange and multipole terms overrule smaller spin-orbit effects, except that scalar-relativistic pseudopotentials will not necessarily give the correct splittings. Interconfigurational energy differences will differ slightly when the radial wave functions are self-consistently determined in a nonsphericalized atomic program, though transferability should not change.

To examine the differences which the forms of exchange and correlation can make on theoretical valence properties predicted by pseudopotentials, we conducted tests on pseudopotentials for various elements: sodium, potassium, calcium, scandium, titanium, silicon, chromium, and nickel. This selection of atoms gave opportunity to test over a wide range of valence properties. Not every element was tested in the same fashion, since exchange and correlation affect valence properties of different elements differently. Among the tests we could perform on the pseudopotentials, once their transferability had been established, were tests of atomic properties such as electron affinities and removal energies, interconfigurational total-energy differences, and molecular binding properties.

Pseudopotential results could be most easily compared to experiment directly when only one electron was in the valence shell. In this case, the exact solution of the system was found by solving the radial wave equation. When more than one valence electron was present, a recent scheme developed by Bachelet, Ceperley, and Chiochetti<sup>9</sup> could sometimes be used to transform pseudopotentials into a fully local pseudo-Hamiltonian compatible for use in diffusion Monte Carlo (DMC) calculations. The pseudo-Hamiltonian after the transformation is exactly equivalent to the original pseudopotential for a single electron in an *s* or *p* state, and a good approximation when more than one valence electron is present.<sup>33</sup> DMC is an exact many-body technique allowing the direct comparison of total energies with experiment, within statistical errors. The computational time to obtain the molecular binding curve (on a Cray Research, Inc., X-MP/48 supercomputer) varied from a few minutes for two-electron systems to a few hours for Si<sub>2</sub>. Since the present formulation of the pseudo-Hamiltonian method is not easily applicable to calcium and transition metals because it cannot represent systems where valence level energies are not monotonically increasing with increasing angular momentum, we did not do many-body tests for those elements. One could also perform configuration-interaction or other many-body calculations for all elements without invoking the pseudo-Hamiltonian procedure, and we are currently carrying out such calculations. However, we are particularly interested in the diffusion Monte Carlo as

it can be used also for calculations on larger systems where comparable configuration-interaction calculations are presently not feasible. In addition, the Monte Carlo method is a simpler and more robust method, and the errors of Monte Carlo calculations can be simply determined. For nickel and chromium, we mainly desired to test the transferability of LDAX or LDAX-SIC pseudopotentials because transferability is particularly difficult for transition metals.<sup>2,34,35</sup>

## Results

### *Sodium, potassium, calcium, scandium, and titanium*

For sodium, potassium, calcium, scandium, and titanium, pseudopotentials generated using a variety of combinations of exchange, correlation, and SIC types were

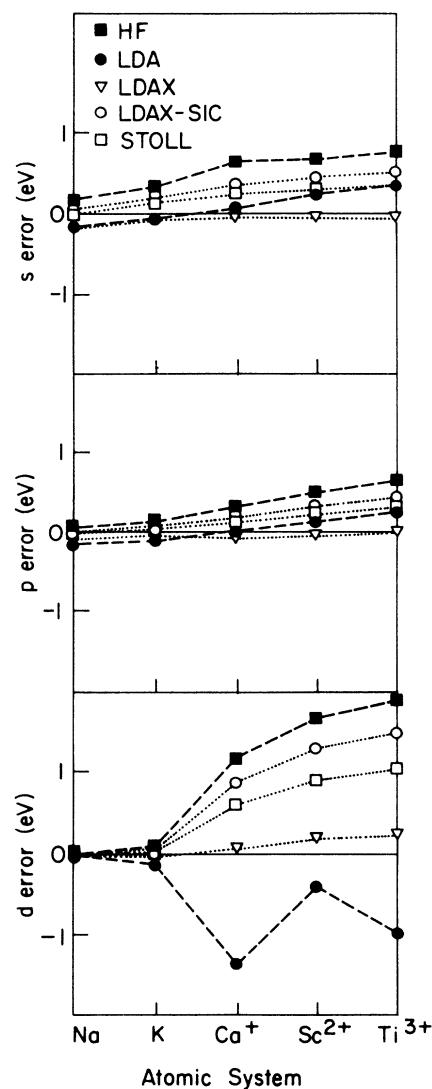


FIG. 1. Errors in removal energy of *s*, *p*, and *d* electrons for various atomic systems, as predicted by pseudopotentials generated with HF, LDA, LDAX, LDAX-SIC, and Stoll's SIC. Experimental data were taken from Ref. 38.

tested for their ability to predict experimental “eigenvalues” of the last valence electrons in the  $s$ ,  $p$ , and  $d$  channels. In Fig. 1, we present errors (comparing with experiment) in the pseudopotential eigenvalues for each element. All pseudopotentials (except LDA) were generated with no valence electrons present; the LDA pseudopotentials were taken from a standard table.<sup>1</sup> This was done because having no valence electrons present corresponds to the frozen single-particle potential which one valence electron in the presence of a bare ion core should “see”. In the LDA, however, such a configuration leads to enormous overbinding of valence states. For example, we found that the  $3d$  state in titanium would have been overbound by about 10 eV. On the other hand, the table of LDA pseudopotentials reduced these errors dramatically, since the table was generated in other configurations. We therefore suggest that one generate LDA pseudopotentials in configurations similar to those used in Ref. 1 if one wishes to use LDA pseudopotentials in subsequent many-body calculations. It can be seen that LDAX was the closest to experiment overall, doing significantly better than both LDA and HF, and also LDAX-SIC. Fig. 1 demonstrates how LDA exchange overbound the  $3d$  levels significantly, for reasons previously discussed. (The LDA results may change when corrections are made for the nonlinearity of local-density exchange.) LDAX-SIC was actually better than LDAX for sodium and potassium, where LDAX was slightly overbinding, though the largest errors for LDAX-SIC taken from the whole set of atoms are much larger than the largest errors for LDAX.

We then proceeded to study electron affinities and

molecular binding properties predicted by the HF, LDAX, and LDAX-SIC pseudopotentials for sodium and potassium. The calculation of the exact two-electron pseudo-Hamiltonian energies was done using DMC. We present our results along with those for HF pseudopotentials by Müller, Flesch, and Meyer<sup>27</sup> as well as for the latter potentials after empirically adding on a core-polarization potential (CPP) fitted both to match experimental ionization potentials and achieve the correct long-range effects of such a term as obtained from the experimental polarizability of the alkali ions. Müller and Meyer accounted for many-body effects in their subsequent pseudopotential calculations by including a configuration interaction treatment for the valence electrons. This should give results like those of DMC for the HF pseudopotential since both methods are in principle exhaustive many-body techniques.

We present these many-body results in Table I, giving the electron affinities, as well as the dissociative energy, bond length, and vibrational frequency for the sodium and potassium homonuclear dimers and dimer cations. These quantities were derived from cubic polynomials fitted to DMC total energies as a function of bond length. Analogous results for LDA pseudopotentials and a method of correcting certain errors in such potentials are to be presented elsewhere.<sup>24</sup> We observe that our HF results and the HF results of Müller and Meyer are very similar, demonstrating that our method of achieving soft but short-range  $p$  pseudopotentials in sodium and potassium did not affect the results. We note that the HF pseudopotentials produced slightly underbound molecules

TABLE I. Electron affinity and molecular properties of sodium and potassium. Electron affinity (EA) in eV, and bondlength  $R_e$  (Å), dissociative energy  $D_e$  (eV), and vibrational frequency  $\omega_e$  ( $\text{cm}^{-1}$ ) for the dimer and dimer cation, according to experiment (Ref. 39 for affinities, Ref. 40 for  $\text{Na}_2$ , Ref. 39 for  $\text{K}_2$ , Ref. 42 for  $\text{N}_2^+$  and Ref. 41 for  $\text{K}_2^+$ ), Müller, Flesch, and Meyer (Ref. 27) using their HF and CPP-corrected HF pseudopotentials, and our HF potential, LDAX, and LDAX-SIC pseudopotentials. DMC uncertainties of affinities and dissociative energies are less than 0.01 eV; bond distances less than 0.01 Å, and vibrational frequencies less than a few inverse centimeters. Zero-point-motion effects on  $D_e$  were included.

	Sodium						
	EA	$\text{Na}_2 R_e$	$\text{Na}_2 D_e$	$\text{Na}_2 \omega_e$	$\text{Na}_2^+ R_e$	$\text{Na}_2^+ D_e$	$\text{Na}_2^+ \omega_e$
Experimental	0.55	3.08	0.75	159		0.99	121
$M + M$ HF	0.54	3.18	0.72	151	3.72	0.97	115
$M + M$ HF-CPP	0.55	3.09	0.74	159	3.60	0.99	121
Present HF	0.51	3.16	0.73	155	3.72	0.98	118
LDAX	0.62	2.92	0.96	184	3.43	1.12	134
LDAX-SIC	0.58	3.11	0.82	156	3.63	1.04	123
	Potassium						
	EA	$\text{K}_2 R_e$	$\text{K}_2 D_e$	$\text{K}_2 \omega_e$	$\text{K}_2^+ R_e$	$\text{K}_2^+ D_e$	$\text{K}_2^+ \omega_e$
Experimental	0.50	3.90	0.52	92	4.4	0.80	73
$M + M$ HF	0.50	4.15	0.53	84	4.80	0.80	67
$M + M$ HF-CPP	0.49	3.94	0.54	92	4.51	0.82	74
Present HF	0.51	4.12	0.52	84	4.82	0.78	70
LDAX	0.60	3.74	0.67	92	4.42	0.92	82
LDAX-SIC	0.53	3.96	0.56	96	4.69	0.83	73

and long bond lengths, and that this must have arisen in part from HF omitting core-valence correlation effects, since all valence-valence correlation effects were included in the molecular pseudopotential calculations. The results presented in Table I show that LDAX pseudopotentials consistently overbound the dimers and gave bond lengths which were too short. LDAX-SIC was the best of HF, LDAX, and LDAX-SIC pseudopotentials for these molecules in terms of determining bond lengths, but still led to an overbound molecule, albeit not as overbound as in the LDAX case. This is consistent with LDAX-SIC having given better results than LDAX for atomic sodium and potassium. The best results by far were obtained by the HF-CPP pseudopotentials, which is understandable since they were semiempirical while all others were strictly *ab initio*, and the HF-CPP were the only pseudopotentials which achieved the correct long-range behavior of the CPP. We also see that overbinding of molecules in all of the schemes usually corresponded to electron affinities being too large, and vice versa.

Overall, we see from the five elements discussed here that HF and LDA have problems describing correlation and exchange effects, respectively, and that even LDAX with or without a SIC is not sufficient for reliably predicting valence properties of atoms. This is important, since small errors (a small fraction of an electron volt) in the valence properties of atomic sodium and potassium corresponded to large errors in their observable molecular properties.

### Silicon

We generated LDAX and LDAX-SIC pseudopotentials for silicon in the spin-polarized  $sp^3$  configuration, and compared the properties of atomic silicon and the silicon dimer as described by our pseudopotentials and a standard LDA pseudopotential, again via the pseudo-

Hamiltonian-DMC approach.<sup>9</sup> For configurations with more than one electron of either spin we used release-node DMC<sup>36</sup> (Ref. 36) to exactly account for antisymmetry. This procedure converged rapidly. In Table II, we tabulate various excitation energies of atomic silicon and properties of its dimer according to the three pseudopotentials and experiment. It appears that the LDA, LDAX and LDAX-SIC pseudopotentials predicted atomic energies with roughly equal reliability. The results for the dimer using the pseudopotentials were also not very different. Thus for silicon there was considerable similarity between the pseudopotentials generated using different single-body techniques, a conclusion that has already been reached by others.<sup>9,20</sup>

### Chromium and nickel

Unlike for other elements, transferability is of greater concern for the iron series. Differences between pseudopotential and full-atomic interconfiguration energies can be several tenths of an electron volt, while in other systems such errors are considerably smaller (at most a tenth of an electron volt). Because of the enormous spatial overlap between the  $3d$  valence shell and the  $3s$  and  $3p$  core shells, the frozen-core approximation is more significant than in other systems for the latter shells. Regarding HF transition-metal pseudopotentials, some workers<sup>34</sup> have found that transferability can be improved by including  $3s$  and  $3p$  shells in the valence shell, thereby generating a "neon-core" rather than an "argon-core" pseudopotential for such elements. The inclusion of the eight tightly bound ( $\approx 100$  eV deep)  $3s$  and  $3p$  is disadvantageous for subsequent valence shell calculations, especially of the many-body type. Others<sup>35</sup> have pointed out that frozen-core errors for the  $3s$  and  $3p$  levels are in fact often cancelled by other errors which arise when generating pseudopotentials. They found that

TABLE II. Atom and dimer properties of silicon. Electron affinity (EA) and various  $s$ - $p$  transfer energies and ionization potentials (IP) for atomic silicon, and bond length  $R_c$  (Å), dissociative energy  $D_c$  (eV) and vibrational frequency  $\omega_c$  ( $\text{cm}^{-1}$ ) of the silicon dimer according to experiment, (Ref. 39 for affinity, Ref. 38 for other atomic properties, Ref. 41 for molecules) and LDAX, LDAX-SIC, and LDA (Ref. 31) pseudo-Hamiltonian-DMC calculations. DMC uncertainties in energies were  $\lesssim 0.1$  eV, bond length  $0.02$  Å, frequency about  $30$   $\text{cm}^{-1}$ . Zero-point motion effects on  $D_c$  were included.

	EA	Atomic properties					3rd IP
		$E_{sp}^3 - F_{\sqrt{2}p^2}$	1st IP	$E_{sp}^2 - E_{\sqrt{2}p}$	2nd IP	$E_{sp} - E_{\sqrt{2}}$	
Experimental	1.39	4.13	8.15	5.47	16.34	6.53	33.46
LDAX	1.28	3.86	7.97	5.41	16.37	6.49	33.33
LDAX-SIC	1.42	3.92	8.12	5.10	16.29	6.45	33.33
LDA	1.39	3.80	8.18	5.08	16.48	6.34	33.62
Dimer properties							
	$R_c$	$D_c$	$\omega_c$				
Experimental	4.244	3.25	511				
LDAX	4.27	3.49	596				
LDAX-SIC	4.35	3.09	550				
LDA	4.33	3.19	480				

changing the shape of the pseudo-valence-orbitals', charge densities to resemble closely those of the full-atomic orbitals' densities restored the transferability of argon-core pseudopotentials. Regarding LDA transition-metal pseudopotentials, Greenside and Schlüter<sup>2</sup> obtained highly transferable argon-core pseudopotentials, but only after including the necessary corrections for the nonlinearity of local-density exchange.

We have found that transferability in chromium and nickel argon-core LDAX pseudopotentials equal to that in neon-core pseudopotentials could be achieved by generating the pseudopotentials in a configuration appropriate for each element. We chose chromium and nickel as representative elements from the first and second half of the iron series, respectively. We generated our chromium pseudopotential in the spin-polarized  $d^4$  configuration and our nickel pseudopotential in the paramagnetic  $d^8$  configuration. In this fashion we were able to produce pseudopotentials with only one  $3d$ ,  $4s$ , and  $4p$  ionic pseudopotential (rather than needing one pseudopotential for

each spin type of, say,  $3d$  electron), but which were fashioned in configurations magnetically similar to the ground states of the respective atoms. While scalar-relativistic calculations will generally not yield the correct spin-orbit splittings, our  $3d$  potentials yielded such terms within a factor of 1.5. Obtaining the correct spin-orbit splittings merely requires generating pseudopotentials using the Dirac equation and following prescribed procedures.<sup>37</sup>

In Fig. 2, we present errors in various excitation energies (comparing to experiment) for full-atomic HF, LDA, LDA-SIC, LDAX and LDAX-SIC and pseudopotential LDAX and LDAX-SIC calculations for chromium and nickel. The transferability of the LDAX scheme (without any nonlinearity terms) is demonstrated by the pseudopotential and full-atomic results tracking each other closely, while the transferability of pseudopotentials generated using other schemes, mentioned above, was established by other workers, with the provision of nonlinearity corrections being applied in the LDA exchange case. Baroni<sup>41</sup> has carried out extensive, restricted, *nonrelativistic* work on the whole iron series, demonstrating that full-atomic LDA-SIC, LDAX, and LDAX-SIC give results in roughly equal agreement with experiment.

Accuracy of the LDA and LDA-SIC schemes arise from the partial cancellation of errors caused by LDA exchange and LDA correlation;<sup>20</sup> errors for the HF and LDAX-SIC methods arise, as stated before, partly because exchange effects are not screened in the case of HF exchange, though such screening is done mostly by valence electrons and can be added later. In the case of LDA exchange pseudopotentials for transition-metal elements, core-valence many-body effects (especially exchange) are not accurately built into the pseudopotential, though such potentials may possibly be used for subsequent many-body calculations if certain corrections are included.<sup>24</sup> In the case of LDAX or LDAX-SIC pseudopotentials, all core-valence many-body effects on valence properties may be reasonably accurately built into the potentials, giving them prospect for use in subsequent many-body calculations without any particular corrections. We have already seen that HF exchange plus a local-density correlation is better than LDA when generating pseudopotentials for elements in the same row towards the very left end of the periodic table, such as calcium, scandium, and titanium. This trend may occur throughout the transition-metal series, though many-body tests for both types of pseudopotentials remain to be carried out to confirm this.

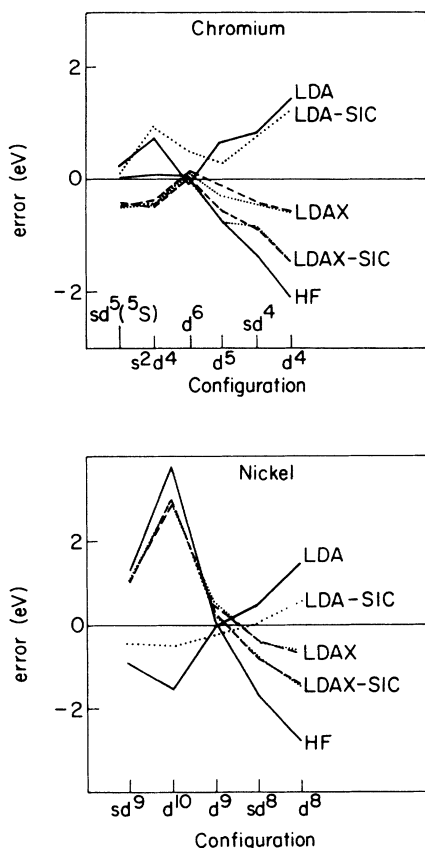


FIG. 2. Errors in excitation energies from the ground state to various configurations compared to experiment in atomic chromium and nickel, which have ground states  $sd^5(^7S)$  and  $s^2d^8$ , respectively. Full-atomic results are given for LDA, LDA-SIC, and HF. For LDAX and LDAX-SIC, we include both full-atomic results (dotted line) and pseudopotential results (dashed line) to demonstrate the transferability of the such pseudopotential. Experimental data were taken from Ref. 44.

## SUMMARY AND CONCLUSIONS

We have compared various combinations of forms of exchange, correlation, and self-interaction corrections used in full-atomic calculations to generate pseudopotentials. Using local-density correlation (sometimes with Hartree-Fock correction) in conjunction with Hartree-Fock exchange has led to the best overall pseudopotentials in this work, over both Hartree-Fock and local-density exchange-correlation pseudopotentials. The generation of such pseudopotentials can be understood as the



carrying over of Baroni's improvements<sup>14</sup> from full-atomic to pseudopotential calculations. It appears that where Hartree-Fock exchange plus local-density correlation and local-density exchange-correlation lead to substantially different results, the former is to be preferred, such as in calcium and the iron transition series, where local-density exchange overbinds  $3d$  electrons, and where local-density exchange pseudopotential transferability is hampered by the nonlinearity of such exchange. Nevertheless we note that all pseudopotentials tested led to some errors in both atomic and molecular binding properties; this can be partly attributed to the inadequacy of finding an accurate and reliable correlation functional and partly to the assumed forms of the pseudopotentials and pseudo-Hamiltonians. Demand for more accurate pseudopotentials may ultimately require a many-body treatment to calculate the full-atomic configurations from which pseudopotentials are generated.

*Note added in proof.* The  $d$ -electron eigenvalue errors plotted in Fig. 1 include errors due to the frozen-core ap-

proximation as well as exchange-correlation errors. The frozen-core errors are strongest in scandium and titanium, where they are  $\sim +0.7$  and  $+0.9$  eV, respectively. This will make all but the LDA curves (for which the pseudopotential was taken from Ref. 1) for  $d$  electrons in Fig. 1 shift down accordingly.

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