

Hardness conserving semilocal pseudopotentials

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A new type of pseudopotentials for local orbital methods is presented. Hardness conserving semilocal pseudopotentials have been generated for all elements from H to Am. The construction is based on a minimization of errors with the norm conservation conditions for 2–3 relevant ionic configurations of the atom. Besides the transferability between atomic states, the portability among density functionals is also of interest. This paper explores if the norm-conservation errors can be kept reasonably small when minimized for two functionals, e.g., the generalized gradient approximation (GGA) and local density approximation, simultaneously. It is found that the errors can be kept at roughly the same low level as for a single functional. Since these pseudopotentials are mainly designed for use with local orbital methods, semicore functions may be treated as valence functions, helping to increase the accuracy and portability. Therefore the name density functional semicore pseudopotential or DSPP is suggested. To further improve portability and, importantly, also aid numerical stability with GGA's, a core density (nonlinear core correction) is used. As with other pseudopotentials, scalar relativistic corrections to atomic scattering properties can easily be incorporated into this PP. Finally performance DSPP's versus all electron DSPP's with the same method, will be shown for an extensive set of test calculations. It is found that the DSPP is a very well behaved pseudo-potential.

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I. INTRODUCTION

Pseudopotentials have a long history both in solid state electronic structure calculations and in quantum chemistry calculations for molecules. It is clear that the pseudopotential (PP) is an additional approximation on top of approximations that are usually made in all electron (AE) calculations, i.e., Born-Oppenheimer approximations, density functional approximations, and truncations of the wave function and orbitals. In solid state plane wave calculations the PP is an essential ingredient to make plane wave expansions converge reasonably fast. PP's designed for plane wave usage normally incorporate semicore states into the core. This is in the interest of fast convergence and at the loss of a more accurate description of the polarizability and magnetic moments due to the shallow core states. The introduction of norm conserving PP's (Ref. 1) was a great step forward toward first principles PP's with improved transferability from one system to another. The norm conservation condition guarantees the exact scattering properties of the ionic core at a particular energy and for a particular electronic configuration of the element. The norm conservation condition can be applied to several angular momentum channels, which leads to a semilocal form of the PP involving projectors. The later development of extended norm conserving PP achieves compliance with the norm conservation property at several energies of the reference state of the element. This further control of scattering properties is particularly important for ultrasoft PP's which further speed up plane wave convergence.

Norm conservation and extended norm conservation emphasize a modeling of the atomic scattering properties in a range of energies for a given potential. Another approach seeks to model the scattering properties of an atom in different charge states. This was initiated by Teter,² emphasizing the importance of hardness for the transferability of the PP. The need to preserve correct atomic scattering properties as a function of occupation was stressed again recently.³

Quantum chemistry PP's were designed for use with localized basis set Hartree-Fock and wave-function methods. Because of the high power of the scaling law for computing time with the number of basis functions in wave-function methods, the elimination of core functions aids greatly in speeding up calculations even on medium sized systems treated with a modest basis set. Quantum chemistry PP's often are made to produce eigenstates which are shape consistent with the tails of AE orbitals.⁴ In these PP's it is well established that semicore functions are not pseudized away.

The present PP's are intended for use with density functional local orbital methods such as the DMol (Ref. 3) approach.^{5,6} Contrary to the requirements of plane wave methods it is desirable to use short ranged PP's. The separability of the PP, which is crucial for efficacy with plane waves, can be abandoned in favor of the more robust semilocal PP's when projectors are to be evaluated in real space. The local orbital approach permits core to keep semicore states as valence functions, which is useful for good accuracy, transferability, and local magnetic moments. It is proposed to call the present PP's "density functional semicore pseudopotentials" (DSPP's). DSPP's can be obtained from the author by email request.⁷

II. FORMALISM**A. Form of the pseudopotential**

The present pseudopotential has a semilocal cusplless form. The PP is localized inside a cutoff radius r_c depending on the element. For each partial wave the external potential is an even polynomial inside the cutoff radius $r_{c,\ell}$. The external potential for the highest partial wave studied becomes the local potential $V_{\text{loc}} = V_{\ell_{\text{max}}}$, and the projector potentials for a partial wave ℓ are then defined as the difference of the external potential for ℓ and the local potential:

$$V_{\text{ps}} = V_{\text{loc}} + \sum_{\ell=0}^{\ell_{\text{max}}-1} |\ell m\rangle (V_{\ell} - V_{\text{loc}}) \langle \ell m|.$$

In the case of a real space evaluation of the projectors with a local orbital basis, the use of separable⁸ PP's would not reduce the operation count. The details concerning the form of the present PP are not essential; they are given here for completeness. The cusplless $V_{\ell}(r)$ functions are conveniently expanded in even Legendre polynomials. At $r_{c,\ell}$ the pseudopotential matches the bare potential $-z^*/r$ up to the third derivative. Because of the boundary condition at $r_{c,\ell}$, the four highest Legendre coefficients $a_{i,\ell}$ need not to be tabulated:

$$V_{\ell}(r) = \sum_{i=0} a_{i,\ell} L_{2i}(r/r_{c,\ell}), \quad r < r_{c,\ell}.$$

The PP is then defined to within tabulation accuracy, e.g. micro-Hartree, which is amply enough. The order for this expansion need not be very high. It is found that a lot can be achieved even with the minimal expansion length: two parameters for each partial wave, $r_{c,\ell}$, and one free Legendre coefficient. Sometimes significant improvement is obtained with more coefficients. The present versions of DSPP's use five free Legendre coefficients.

It was opted to include a core density⁹ to improve transferability and magnetic properties. In addition, the core density avoids the occurrence of a very small electron density near the nucleus, a situation which sometimes may lead to numerical problems with gradient dependent density functionals. A few parameters are sufficient to define the important tail region of the core density. The model core density is thus defined as

$$\log[\rho_c(r)] = \sum_{i=1}^n c_i (r/r_d)^{2-i}, \quad r > r_d$$

outside the core density matching radius r_d . The coefficients are determined by a least squares fitting to the core density of the all electron calculation. For $r < r_d$ the model core density is an even polynomial determined from the matching conditions up to the third derivative.

B. Reference states

The pseudopotential should give a good approximation of the scattering properties of all atomic states of interest. In particular it should properly represent the change of an atom under charge transfer. This can be seen as a conservation of hardness. The basic such quantity is the absolute hardness of an atom, defined as $\eta_0 = (I - A)/2$, half the difference of the ionization potential and the electron affinity.¹⁰ In order to define charge states of particular practical relevance to calculations of compounds it is useful to remember how effective localized basis sets can be constructed.⁵ The variational basis functions must span an appropriate function space to describe an atomic response to charge transfer. The polariza-

tion functions are chosen to describe an atomic response involving partial waves in unoccupied orbitals. Two criteria guide the actual selection of basis functions: (a) the total energies of a reference set of molecules should be minimized for a given basis set size, and (b) the basis functions must not give rise to a near singular overlap matrix or have otherwise pathological properties. This can be fulfilled very well by deriving the variational basis function set from the neutral atom and from positive ions.⁵ It seems natural to take the same ionic states, that are useful for generating basis functions, as atomic reference configurations to define the scattering properties for the PP.

For light atoms the most effective d -polarization functions were found to be of Slater type form. For PP reference states use of ionic states is preferred. With that exception the choice of reference states follows closely the choice for variational basis functions for double numerical set plus polarization function.⁵

For the generation of reference states as well as for the pseudo partial waves a standard numerical density-function-theory spherical atom program is used. Some details pertaining to gradient dependent functionals was given in Ref. 6. Our program relies on the predictor corrector method and normally uses 501 radial mesh points to solve partial wave differential equations. In a similar spirit it is tried here to span the variations of reference states across a class of density functionals by optimizing the PP's simultaneously for two representative functionals.

C. Norm conserving condition

In the present approach bound atomic configurations are always used as reference states as in most construction methods for PP's. The original formulation of norm conserving properties¹ by Hamann, Schlüter, and Chiang (HSC) allows for scattering type partial waves: (1) real and pseudo valence eigenvalues agree, (2) real and pseudo partial waves agree beyond some r_c , (3) real and pseudo charge densities integrated out to $r > r_c$ agree, and (4) the logarithmic derivative of real and pseudo partial waves and their first energy derivative agree beyond r_c .

As described by HSC properties (1)–(4) are related. In the case of bound states, these properties can be obtained by a simplified set of conditions. Since the bound state can be normalized, agreement at some sufficiently large radius r_b implies a fulfillment of conditions (2) and (3). r_b is always chosen at (or larger than) the largest radius of classical turning point for the orbitals of interest. The bound state orbitals are all decaying beyond that point and the self consistent potential is equal to the all electron potential. Property (4) must be fulfilled on the basis of the Shaw-Harrison-Lüders (Refs. 11 and 12) sum rule discussed by HSC. This property guarantees that partial waves behave properly in the vicinity of the reference energy used for the construction of the PP. Extended norm conservation requires partial waves of the same potential to fulfill the properties at a set of energies. This can be obtained in the framework of an ultrasoft PP construction.¹³ Here we attempt to fulfill norm conserving conditions for different ionic configurations of an atom. This

amounts to seeking hardness conserving PP's.² The closest approximation to such a PP must be sought by an optimization procedure. With the optimization, information on the transferability of the PP is gained as a byproduct.

D. Optimization

The target function to be minimized is chosen as the rms deviation from the norm conserving conditions for the set of target states,

$$D_0^2 = \frac{1}{2N_t - 1} \sum_{\alpha} (\epsilon_{\alpha}^{ps} - \epsilon_{\alpha})^2 + [\phi_{\alpha}^{ps}(r_b) - \phi_{\alpha}(r_b)]^2, \quad (1)$$

where α is a combined index which enumerates valence and polarization orbitals for the ionic configurations and functionals under consideration as the target set. The target set consists of N_t pairs $\epsilon_{\alpha}, \phi_{\alpha}(r_b)$. The first term aims to make the pseudoeigenvalues ϵ_{α}^{ps} agree with the all electron ones. The second term relates to the charge conservation by comparing the pseudo and real amplitudes at r_b , according to the discussion in the Sec. II C. D_0 gives an idea of the accuracy of the pseudoeigenvalues (in atomic units) and less directly on the charge conservation across the target set. In principle one might introduce weight factors for the two kinds of terms entering D_0 . If atomic units (a.u.) are chosen, the magnitudes of either term are of the same order and a reasonable ratio of the weights should be of order unity. Therefore the weights for the calculation in a.u. were chosen to be equal to 1. Other reasonable choices of the weights do not lead far away from a local minimum found with the unity weights. Properties remain so similar to the original DSPP that further investigation was dropped. The basic problem appears to be that no perfect transferability among different charge states can be obtained within the class of semilocal PP's.

It turned out to be necessary to add penalty functions to the target function to prevent the optimization from being trapped in an undesirable local minimum. The penalty functions used here are designed to vanish exactly for the class of desired PP. The desirable properties and the associated penalty function are discussed below. It is desirable that the cutoff radius r_c of the PP not be too large. The matrix element between two localized basis functions is generally non-vanishing if the two functions can interact via a PP: $\langle \phi_i | V_{\text{nonloc}} | \phi_j \rangle \neq 0$ if $|\mathbf{r}_i - \mathbf{r}_j| < r_{c,\phi_i} + r_{c,\phi_j}$ and $|\mathbf{r}_j - \mathbf{r}_V| < r_{c,\phi_j} + r_{c,V}$. The short ranged character of the present pseudopotential is useful to achieve good accuracy. At the same time it aids in a speedy evaluation of matrix elements in real space. For the present hard PP, a dual space representation (real and reciprocal space) (Ref. 14) would still not make DSPP's very appealing for plane wave methods. To put the cutoff radius under control, a penalty function is introduced:

$$D_{1,\ell} = \begin{cases} w_1(r_{c,\ell} - r_{\text{max}}) & \text{if } r_{c,\ell} > r_{\text{max}} \\ 0 & \text{if } r_{c,\ell} \leq r_{\text{max}} \end{cases} \quad (2)$$

A value $w_1 = 10^4$ a.u. was used. The cutoff radius of the PP must not be smaller than the radius of the outermost node to

be pseudized. However, no penalty function needed to be introduced for this. A cusplless PP need not be very strong. It should not be, because strong variations of the PP may create high Fourier components for the orbital which may require additional numerical effort. That should be spent only if the strong PP is physically well motivated. The penalty below helps to guide the optimization toward PP's which are in the range of function values $[V_-, V_+]$,

$$D_{2,\ell} = w_2 \int_0^{r_{c,\ell}} p[V_{\ell}(r)] dr,$$

where w_2 is a weight factor and the function $p(V)$ is defined as

$$p(V) = \begin{cases} (V - V_+)^2 & \text{if } V > V_+ \\ (V - V_-)^2 & \text{if } V < V_- \\ 0 & \text{else.} \end{cases} \quad (3)$$

The optimization of the PP might go astray and end up with a wiggly function for the potential $V_{\ell}(r)$ acting on scattering channel ℓ . This is not desirable. The optimization can be guided by a penalty function involving a measure of the wiggleness. A measure of wiggleness for a function $V(r)$ is

$$J = \int_{r_1}^{r_2} [V''(r)]^2 dr, \quad (4)$$

where the integral is taken in principle from the origin to $r_{c,\ell}$. However, with this basic definition only a linear function of the radius in each channel would go without penalty. One needs to exclude from the penalty function the type of curvature that must necessarily appear in V_{ℓ} for an acceptable PP. If a partial measure J_i is taken between subsequent turning points separately, a suitable measure of wiggleness can be defined. The cusplless form of the PP leads to at least one turning point in the interval $[0, \infty]$. If the PP for a partial wave is repulsive near the core, two turning points necessarily appear. Therefore, the penalty function is defined to vanish for up to two turning points between $r=0$ and $r=r_{c,\ell}$. If there are more than two turning points $n_w > 2$ the measures J_i are added up, except for the two end parts and for the largest intermediate part J_m :

$$D_{3,\ell} = \begin{cases} w_3 \left(\sum_{i=2}^{n_w-1} J_i \right) - J_m, & n > 2 \\ 0 & \text{else.} \end{cases} \quad (5)$$

The total target function for each element is D (PP parameters) $= D_0 + \sum_{\ell} D_{1,\ell} + D_{2,\ell} + D_{3,\ell}$, where the sum over ℓ should run over the projector channels and include the local potential once. The local potential acts on all partial wave channels beyond the maximum projector channel. The minimization is done using the downhill simplex method. It was found that increasing the Legendre expansion order step by step using the converged lower order PP as a startup is a

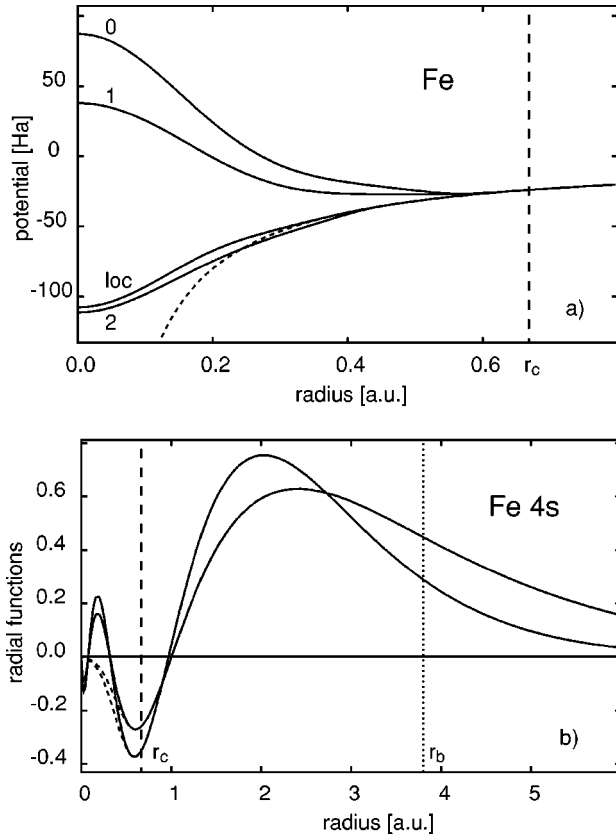


FIG. 1. (a) DSPP_s_PBE for Fe: external potentials for s , p , d , and all higher ℓ partial waves. Also shown is the z^*/r potential for $z^*=16$. (b) Pseudo radial functions for a neutral atom and for $2+$ ion. Shown are the cutoff radius r_c of the PP and the radius r_b , where the matching of the partial wave amplitude is measured. The inner maximum belongs to the radial function for a positive ion, the outer maximum to the neutral atom.

reasonably robust procedure. As mentioned above, the contribution of the penalty function $D_1 + D_2 + D_3$ always becomes small when compared to D_0 for the completed optimization. Usually the value of the penalty function at the optimum is zero.

The primary density functional used here to define the AE reference is the Perdew-Burke-Ernzerhof (PBE) functional.¹⁵ This is a functional with an explicit dependence on the density gradients. Koelling Harmon scalar relativistic average radial equations¹⁶ are used to define AE radial functions. For the corresponding PP the abbreviation DSPP_s_PBE is used. In attempting to span a large class of functionals a local density functional approximation (LDA) in the form of the Perdew Wang local correlation¹⁷ (PWC) plus local exchange functional is used to define the duplicated set of target orbitals. For this two functional scalar relativistic PP's the abbreviation DSPP_s is used.

Some of the points raised above are illustrated in Fig. 1(a), which shows the external potentials acting on each partial wave. The external potentials match smoothly with the z^*/r bare potential at the cutoff radius $r_{c,\ell}$. The local potential acts on all partial waves from ℓ_{\max} up. The projector

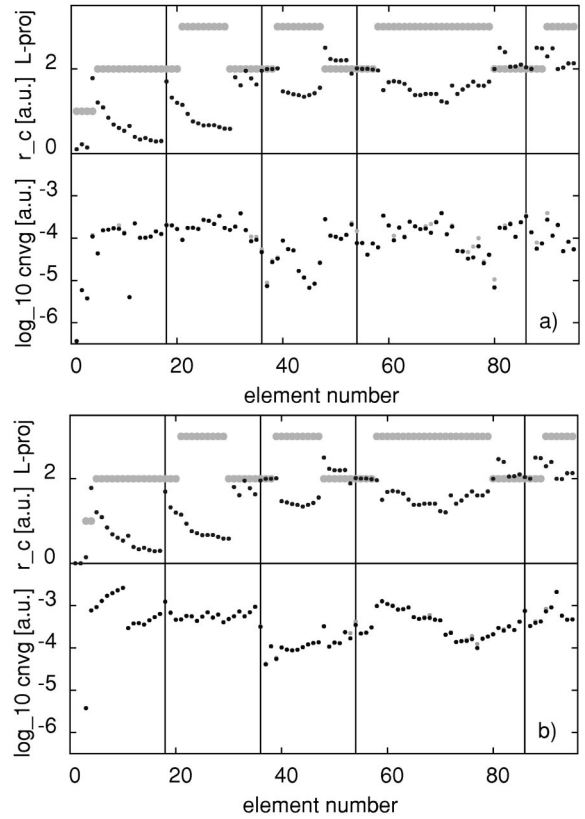


FIG. 2. Characteristics of DSPP (a) scalar relativistic pseudopotential for optimized for the PBE functional (DSPP_s_PBE) (upper part); black dots: cutoff radius; gray dots: number of ℓ projectors; lower part: accuracy measure for the PP of each element; black dots: excluding penalty function; gray dots: accuracy measure including penalty function. (b) For DSPP_s the information is similar to (a), but the PP is targeted for two functionals: PBE and PWC.

functions are the differences $V_\ell - V_{\text{loc}}$ and vanish at r_c . Figure 1(b) shows the s partial wave for the atom and a ionic state. Outside r_c all-electron and pseudopartial waves are almost identical. The figure suggests that the exact value of r_b , where the amplitude difference is minimized, is not critical. Figure 2 shows the minimized values of the target function D for scalar relativistic radial functions. Also shown is the value of the PP cutoff radius and the ℓ value associated with the local part of the PP for each element. The lower part in each panel shows that D is of the order of 0.001 a.u. or smaller for most elements. In fact D and D_0 are shown, but for most elements only a single point can be seen on the graph. The comparison of panels (a) for a single functional PP and (b) for two functionals spanning from the LDA to the generalized gradient approximation (GGA) suggests that (b) is somewhat less close to fulfilling norm-conserving conditions. The application tests below will show, however, that the degradation of the PP due to the functional-portability requirement is not important. The elements C–Ne for DSPP_s are all above 0.001 a.u., which says that the norm conserving conditions have been fulfilled less precisely than for almost all other elements. A choice may be to treat the elements up to Ne with the all electron approach, especially since only the $1s$ core is pseudized in Be–Ne. A cusplless all

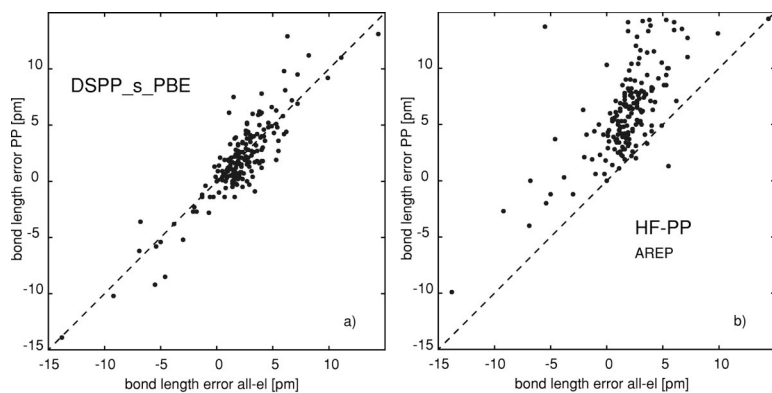


FIG. 3. (a) Bond length errors with DSPP_s_PBE vs errors with all-electron calculation for functional PBE. (b) Same for AREP.

electron PP can be (and has been) constructed for H–Li, but there appears to be no advantage using such a PP with local orbitals. It is interesting to note that the minimum $D(N)$ reached for the $2p$, $3d$, and $4f$ elements is larger in value, and thus less good, than for the p , d , and f elements with higher principal numbers. For some elements it appears to be difficult to obtain equally low minima as for neighbor elements: e.g., Cd (48). This obviously depends on the configurations used to define the target function. Not surprisingly, it was found that the value of the minimum can be reduced by choosing target configurations with smaller differences of ionicity. Thus Fig. 2(a) gives information on the transferability among ionic states, and Fig. 2(b) contains information on transferability among functionals in addition. The tests on PP performance in the following section should set the right expectations for applications.

III. PERFORMANCE OF DSPP

A. Molecules

There is a number of diatomic molecules for which accurate spectroscopic data are known. For the present benchmarking purpose we select the diatomic molecules where data sets of bond length, ground state vibrational frequency, and dissociation energy are known experimentally. Most of these data can be found in the review of Huber and Herzberg.¹⁸ Some more molecules for which similarly good data are available have been added to the data set, notably Cr_2 and Mo_2 .^{19,20} In the case of Ag_2 an estimated bond length of 252 pm is used. This test set consists of a total of 201 cases. 117 are treated with the spin unrestricted functional. The unrestricted case includes also antiferromagnetic

singlet states which are handled allowing $C_{\infty, V}$ symmetry for the spin dependent part of the effective potential. The test set includes furthermore 30 cations and 15 anions.

Since this test set provides well established experimental data, it is interesting to put the inaccuracies for calculated properties using the pseudopotential in perspective with the errors for the all electron calculation. The numerical errors are small as compared to the ones from the approximate density functionals that can be used in practical calculations.

Figure 3 shows a correlation plot for errors of calculated bond length with DSPP_s_PBE. against errors from the all electron calculation with the PBE functional. The all electron calculations incorporate scalar relativistic corrections.²¹ If the points in the figure are perfectly aligned along the diagonal, this would mean that errors from the PP would be negligible against the errors still present in the all electron calculation. The errors in the present all electron calculation are clearly dominated by approximations due to the functional. The majority of points in the plot falls near the diagonal. This means that the largest error on average is from the functional. The errors from the PP are smaller, but non-negligible. The graph suggests that the DSPP results have no significant bias as compared to the all electron results. There are 12 cases where the difference of calculated bond length between PP and all electron exceeds 3 pm. The largest difference occurs for Cr_2 . Incidentally, the DSPP bond length is closer to experiment on average. For a statistical analysis, cases with bond lengths differing more than 10 pm from experiment are considered outliers. In this analysis the mean deviation of PP vs AE is -0.2 pm and AE vs exp $+1.8$. rms deviations are 1.6 and 3.4 pm, respectively. When such a graph is plotted for a semicore PP derived from Hartree Fock

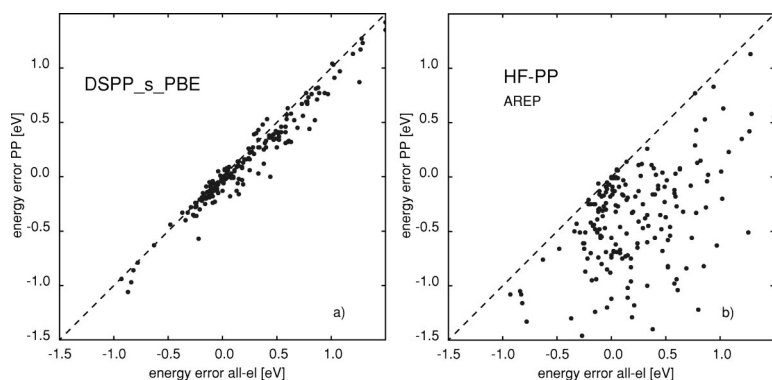


FIG. 4. (a) Binding energy errors for 201 diatomic molecules with DSPP_s_PBE vs errors with all-electron calculation for functional PBE. (b) Same for AREP.

TABLE I. Performance for a test set of 148 neutral molecules in kcal/mol.

Calculation	Mean error	rms error	Abs. avg. error
All electron	0.9	7.7	5.8
DSPP_s	-2.0	7.5	5.8
DSPP_s_PBE	-3.1	8.0	6.3
TMPP	3.9	12.1	9.6

(HF) atomic calculations,^{22,23} a systematic bias is found as shown in Fig. 3(b) for the average relativistic effective core potential (AREP). The bond length turns out to be systematically large, the binding energies too small and the vibrational energies too small. For this set of diatomic molecules a HF derived semicore PP represents a major approximation with an error somewhat larger than the one from the generalized gradient approximation.

Figure 4 correlates PP errors in the binding energy (D_0) against the respective errors for an all electron calculation with the PBE functional. The data points scattered along the positive diagonal show that for many of these molecules the PBE functional overestimates the binding energy. The correlation of errors between PP and all electron cases is very close. The PP has a slight tendency to overestimate bond energies less, which is nice, superficially. There are nine cases where the difference in binding energy exceeds 0.3 eV. The largest case is N_2 ; the PP result happens to fall very close to the experimental value. The inaccuracies introduced by the PP should be put in perspective with the errors for the PBE functional. The figure clearly shows an accumulation of points along the diagonal, with a number of cases overbound. A smaller number of cases turns out under-bound as compared with experiment. Figure 4(b) shows the correlation of binding energy errors with AREP PP against the AE errors. The AREP errors involve error components to be ascribed to the PP which are of the same magnitude as the ones from the density functional.

The value of the vibrational frequency ω_e has been calculated in a harmonic approximation for this survey. If outliers involving errors greater than 100 cm^{-1} are not counted, one finds a mean error of -7 cm^{-1} and an rms error of 35 cm^{-1} . The difference from all electron frequencies is, again excluding outliers, mean $+7$ and rms 24. The errors with respect to experiment happen to be slightly larger with

all electron calculation than with PP. This means that PP errors for DSPP's partially compensate for functional errors for the PBE functional. The results for DSPP_s are vexingly similar to the ones calculated with the DSPP_s_PBE; therefore, no extra figures for DSPP_s are shown here.

The test set proposed by Curtiss *et al.*²⁴ consists of 148 neutral molecules with well established enthalpies of formation (the G2 set). The heaviest element in that set is Cl. The importance of elements by number of occurrences is H, C, O, F, Cl, N, S, Si He, Ne, and Mg do not occur. This test set emphasizes the elements for which the quality measure of the present construction procedure is not pleasingly good in case of the DSPP_s. The test is done using fixed MP2 geometries²⁴ and scaled HF frequencies²⁴ for thermal corrections. Here the performance of the BECKE88 (Ref. 25) PERDEW91 (Ref. 26) (BP) functional is compared between all electron and DSPP calculations. Table I shows a comparison. It is clear from the table that the error characteristics with all-electron or with DSPP calculations are very similar. For comparison Troullier-Martins pseudopotentials (TMPP's) (Ref. 27) were used for this test. Performance is less good than for DSPP's. The most important differences with the DSPP are that the TMPP has a significantly larger cutoff radius of the PP, which may affect accuracy for the short molecular bonds in this test set. For the heavier atoms Al-Cl more electrons are pseudized in the TMPP. Figure 5(a) shows the correlation of DSPP errors vs AE errors for the G2 test. The points remain in an area close to the diagonal indicating predominance of errors due to the functional. For the TMPP [Fig. 5(b)] an error of larger magnitude than with DSPP shows up. This is also shown by the summary numbers in Table I.

B. Solids

Monoelemental simple solids provide a useful testing ground to put PP errors into perspective with the density functional approximation. The calculations were done with shifted k -point meshes of even order. The default⁶ resolution in k -space results in an 8 8 8 Monkhorst Pack mesh for Fe, Ni, etc., and a 4 4 4 mesh for Cs. The atomic cutoff parameter was set to $(6.5 \times V)^{1/3}$ (a.u.), where V is the atomic volume. This yields $R_c = 6.3$ a.u. for diamond, 8.0 a.u. for Fe, and 16.9 a.u. for Cs. Experimental data are taken from Kittel²⁸ and the inorganic crystal structure data base.²⁹ The results in Table II suggest that the two PP's presented here

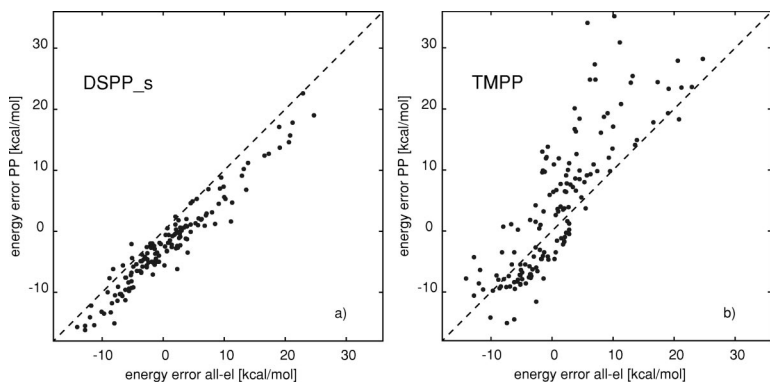


FIG. 5. (a) Binding energy errors for a G2 set of 148 neutral polyatomic molecules with DSPP_s vs errors with all-electron calculation for functional B88P91. (b) Same for Troullier-Martins PP (23.061 kcal/mol = 1 eV).

perform almost equally. The DSPP's produce a 0.5% average stretching of the calculated lattice constant as compared to the all electron calculation with scalar relativistic corrections.²¹ The average error of the all electron calculation is +0.4%. The rms error is near 1.5% for DSPP and all electron calculations. The LDA leads to a 2.4% contraction as compared to the experimental reference data, and the LDA rms error is at 2.9%. The difference between the PP and all electron results is significantly smaller than the difference between LDA and GGA functionals. Certain lattice constants from the PBE functional appear to be off by an alarming amount. The one of gray tin is notable +2.9%. For comparison the value from FLAPW (full potential linearized augmented plane wave density functional method) with PBE functional³⁰ is +3.4%. In the case of gold there is a large difference between the DSPP (+2.6%) and the scalar relativistic all-electron result (-1.3%). In this case the FLAPW value³⁰ of +3.2% and the DSPP value are again close.

A further test set consists of elemental semiconductors and zinc-blende semiconductor compounds. The same default parameter settings as for elemental solids were used for these calculations. The average error with the PBE functional using all electrons with scalar relativistic corrections is +1.8% with a rms value of 2.0%. The values with both DSPP's are very similar: +1.8% average and 2.0% rms; the rms difference with the all electron calculation is 0.7%. This can again be put into perspective with PWC-LDA all electron calculations which estimate lattice constants too short by -0.8% on average with an rms error of 1.3%; the rms difference with respect to PBE calculations is 2.9%. Percent errors of calculated lattice constants as compared to the experimental lattice constant are shown in Table III. The rms difference between all electron and DSPP calculations arises mainly from outlier HgSe. The difference between DSPP and AE calculations for the Hg compound may again be due to a shortcoming of the scalar relativistic corrections similar to the gold solid seen in Table II. The semiconductor crystals have been an application area for PP's for a long time. For a comparison with existing pseudo-potentials, TMPP with non-linear core corrections were generated for the PBE functional using the FHI98PP program^{31,32} with default settings otherwise. Table III also shows errors for lattice constants with this TMPP. The TMPP calculation differs from the AE calculation by 1.5% rms, while the DSPP calculation differs by 0.8% rms.

Among the semiconductor vibrational properties, vibrations at the X point appear to be particularly sensitive to PP approximations. GaAs appears to be a bad case, with a tendency to show spurious soft phonons at X in PP calculations. This can be traced back to the relatively strongly attractive potential showing up in the d partial wave channel. By default, the d channel would also define the local potential for the present PP constructs. These spurious vibrational properties were eliminated by introducing an f -channel potential which is less attractive than the one for the d channel. The f potential is taken as the local potential acting on all higher partial waves. This type of modification was introduced for elements As, Se, and Br. Phonons were calculated at special points in the Brillouin zone for all semiconductors studied

TABLE II. Experimental lattice constants and errors (%) for calculated lattice constants for monoatomic solids, (b) bcc, (f) fcc, and (h) hcp stacking sequences changed to cubic fcc (fcc lattice const shown). DSPP_s, DSPP_s_PBE, and all electron calculations, all with a PBE functional. Last column: all electron calculation with, PWC functional; see the text.

			$A(\text{\AA})$	DSPP_s	DSPP_s_PBE	AE PBE	AE PWC
3	Li	b	3.4910	-0.14	-0.14	-0.11	-2.90
4	Be	h	3.1885	2.21	2.27	-0.39	-1.52
11	Na	b	4.2250	0.14	0.13	-0.08	-3.82
12	Mg	h	4.5301	0.11	0.13	-0.07	-1.61
13	Al	f	4.0500	0.00	0.00	-0.78	-1.92
19	K	b	5.2250	0.74	0.90	0.75	-3.39
20	Ca	f	5.5800	1.77	1.78	0.06	-2.05
21	Sc	h	4.6384	-1.01	-1.00	-0.36	-3.64
22	Ti	h	4.1342	-0.60	-0.71	-0.30	-3.14
23	V	b	3.0300	-1.45	-1.40	-1.09	-3.25
24	Cr	c	2.8800	-0.48	-0.48	1.67	-2.78
26	Fe	b	2.8700	-0.41	-0.77	-1.17	-3.92
27	Co	h	3.5413	1.00	0.95	0.47	-3.18
28	Ni	f	3.5200	0.80	0.77	0.49	-2.55
29	Cu	f	3.6100	0.86	0.91	0.78	-2.61
30	Zn	h	3.9293	1.17	1.16	0.50	-3.39
37	Rb	b	5.5850	2.02	2.02	0.86	-4.04
38	Sr	f	6.0800	1.22	1.20	-1.04	-4.96
39	Y	h	5.0901	-0.65	-0.64	-0.40	-3.62
40	Zr	h	4.5317	1.06	1.00	0.56	-2.08
41	Nb	b	3.3000	0.38	0.36	0.71	-1.42
42	Mo	b	3.1500	1.00	0.99	1.08	-0.57
43	Tc	h	3.8533	1.15	1.14	0.84	-0.73
44	Ru	h	3.7901	1.36	1.40	0.94	-0.77
45	Rh	f	3.8000	1.63	1.59	1.13	-0.85
46	Pd	f	3.8900	2.13	2.07	1.76	-0.98
47	Ag	f	4.0900	2.46	2.43	1.78	-1.99
48	Cd	h	4.4216	3.81	3.72	2.30	-2.34
55	Cs	b	6.0450	3.31	3.36	1.59	-4.37
56	Ba	b	5.0200	-1.58	-1.65	-1.80	-6.05
64	Gd	h	5.0906	0.13	0.06	-0.59	-5.00
71	Lu	h	4.9015	0.03	-0.01	-0.72	-4.67
72	Hf	h	4.4649	-0.25	-0.31	-0.81	-3.70
73	Ta	b	3.3000	0.01	-0.01	-0.84	-3.06
74	W	b	3.1600	0.51	0.56	-0.66	-2.11
75	Re	h	3.8896	0.79	0.77	0.39	-1.01
76	Os	h	3.8298	0.91	0.91	-0.03	-1.41
77	Ir	f	3.8400	1.03	1.06	0.28	-1.26
78	Pt	f	3.9200	1.75	1.78	-0.41	-2.28
79	Au	f	4.0800	2.64	2.65	-1.26	-3.72
81	Tl	h	4.8553	3.12	3.14	5.59	-0.39
82	Pb	f	4.9500	2.12	2.23	3.59	-0.30
90	Th	f	5.0800	1.07	1.04	-1.32	-3.83

here, and were found to be in good agreement with AE calculations and the available experimental data. Phonon dispersion relations for GaAs calculated with PBE and DSPP_s_PBE are shown in Fig. 6. Phonons were calculated

TABLE III. Experimental lattice constants and errors (%) for calculated lattice constants for zinc blende semi-conductor crystals. Calculations with DSPP_s, DSPP_s_PBE, and TMPP, including nonlinear core corrections, and all electron with PBE functional and last column all electron with PWC functional; see the text.

PP: functional:	A (Å)	DSPP _s	DSPP _s_PBE	TMPP c_PBE	AE PBE	AE PWC
Group IV						
C	3.5670	0.22	0.25	0.21	0.20	-0.98
Si	5.4300	0.74	0.77	0.14	0.78	-0.45
Ge	5.6580	0.99	1.02	1.43	2.06	-0.40
Sn	6.4900	2.95	2.93	1.42	2.93	0.11
III-V						
AlP	5.4200	1.63	1.65	1.41	1.70	0.28
AlAs	5.6200	1.71	1.73	1.47	1.99	0.15
AlSb	6.1260	1.67	1.67	1.31	1.64	-0.36
GaP	5.4499	0.81	0.81	2.72	1.29	-0.80
GaAs	5.6531	1.13	1.14	3.23	1.86	-0.67
GaSb	6.0950	2.34	2.33	3.55	2.29	-0.44
InP	5.8610	1.64	1.76	3.03	2.07	-0.25
InAs	6.0583	1.78	1.88	3.17	2.45	-0.14
InSb	6.4782	2.75	2.85	3.43	2.83	-0.01
II-VI						
ZnS	5.4145	0.92	0.92	2.55	0.99	-1.78
ZnSe	5.6700	1.37	1.41	2.87	1.61	-1.29
ZnTe	6.0980	2.29	2.26	3.13	1.90	-1.07
CdS	5.8100	2.52	2.53	3.94	2.49	-0.50
CdSe	6.0770	2.44	2.47	3.75	2.60	-0.47
CdTe	6.4800	3.42	3.39	3.96	2.83	-0.33
HgSe	6.0840	3.64	3.68	4.15	0.64	-2.46
I-VII						
CuCl	5.4203	0.70	0.66	3.23	0.78	-3.35
CuBr	5.6840	1.60	1.52	3.44	1.41	-2.55
CuI	6.0590	1.82	1.79	3.69	1.53	-2.14
AgI	6.4950	4.12	4.11	4.93	3.39	-1.00

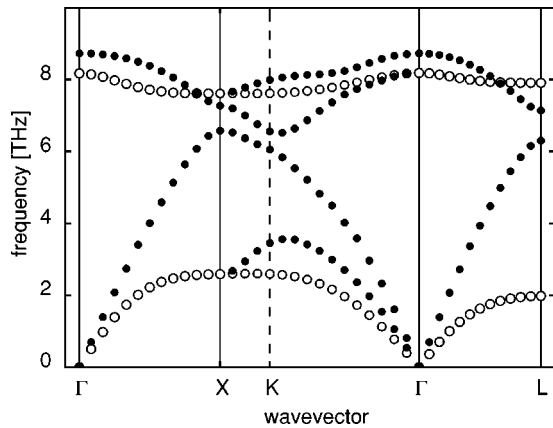


FIG. 6. Phonon dispersion relations for GaAs, with PBE functional and DSPP_s_PBE. Transverse polarization: hollow symbols, longitudinal polarization or mixed along (110) X-K-Γ: full symbols.

TABLE IV. Frequencies of some selected modes for GaAs (THz). Also shown is the bulk modulus B (GPa).

Mode	Wave vector	exp	DSPP_s_PBE	PBE AE	PWC AE
TO	Γ (0,0,0)	8.02	8.18	8.22	8.11
LO	Γ (0,0,0)	8.55	8.73	8.88	8.78
TA	X (1,0,0)	2.36	2.59	2.25	2.48
LA	X (1,0,0)	6.80	6.58	6.70	6.68
LO	X (1,0,0)	7.22	7.28	7.21	7.15
TO	X (1,0,0)	7.56	7.61	7.76	7.56
TA	L (.5,.5,.5)	1.86	1.98	1.81	1.92
LA	L (.5,.5,.5)	6.26	6.30	6.22	6.25
LO	L (.5,.5,.5)	7.15	7.14	7.24	7.10
TO	L (.5,.5,.5)	7.84	7.91	8.00	7.88
B		76	63	60	80

with the frozen phonon approach at the experimental lattice constant using suitably shaped supercells for the three sub-panels in the figure. The longitudinal optical (LO) frequency at Γ was taken as the numerical $q \rightarrow 0$ limit. A comparison between experiment and calculations of PP and AE types can be seen in Table IV. Agreement of calculated frequencies in the Table IV with experiment is consistently better than 5% and typically near the 2% level of agreement. The transverse acoustical (TA) mode at the X point in reciprocal space is particularly sensitive. Also shown is the bulk modulus.

TABLE V. Lattice constants for rock salt structure ionic compounds. Errors in percent as compared to exp lattice constant for DSPP_s, DSPP_s_PBE, AE PBE, and AE PWC calculations.

	A (Å)	DSPP_s	SPP_s_PBE	AE PBE	AE PWC
LiH	4.0834	-1.99	-1.86	-1.99	-5.11
LiF	4.01	1.31	1.53	1.27	-1.46
LiCl	5.11	0.90	0.91	0.79	-3.26
LiBr	5.46	1.91	1.42	1.46	-2.68
LiI	5.95	1.81	1.82	1.53	-1.89
NaH	4.89	-1.65	-1.59	-1.96	-2.43
NaF	4.61	2.14	2.22	2.16	-1.91
NaCl	5.60	2.33	2.34	2.32	-1.80
NaBr	5.93	2.50	2.33	2.18	-1.50
NaI	6.41	2.30	2.32	2.05	-2.01
KF	5.31	2.07	2.18	2.26	-2.42
KCl	6.25	2.11	2.11	2.39	-2.44
KBr	6.54	2.57	2.69	2.72	-2.32
KI	6.99	3.43	3.41	3.45	-1.93
RbF	5.59	2.82	2.83	2.17	-2.33
RbCl	6.53	3.00	3.00	2.81	-2.02
RbBr	6.82	3.70	3.56	3.05	-1.94
RbI	7.26	3.80	3.79	3.15	-1.74
AgCl	5.5490	1.91	1.91	1.84	-2.95
AgBr	5.7403	2.86	2.89	2.50	-2.09
PbS	5.9340	1.41	1.47	2.55	-0.82

Ionic compounds present an interesting test for the transferability of the atomic scattering properties to the ionic state, see Table V. This may also be termed hardness conservation. The PBE functional overestimates the lattice constants with the notable exception of the hydrides LiH, NaH. The overestimation is 1.84% on average for the AE calculation and 1.96% for the DSPP; the rms deviation from experiment is 2.4% and 2.5%, respectively. The rms deviation for both DSPP's from AE is 0.4% in this set of compounds. There is nearly a constant difference of 4.1% between PBE and PWC results, again showing the importance of the functional approximation. There is a systematic trend in computed results tending to yield larger lattice constants as compared to experiment when heavier elements are involved.

IV. CONCLUSIONS

A hard pseudopotential (PP) suitable for local orbital methods is presented. Such PP's have been constructed and tested here for all elements from H to Am. The author recommends using all electron calculations for light elements. For elements from Tl, Pb... up, the neglect of spin-orbit corrections is expected to be a more important approximation than for the other elements. The main emphasis is on accuracy, so semicore states are left as valence states to a large extent. In addition, a model core density correction is used to maintain a realistic total density profile near the nucleus. This helps to make gradient dependent functionals behave well. For good portability among different ionic states, hard-

ness conservation was built in by optimizing the PP for an atomic configuration and at least one ionic configuration. For portability between functionals two representative functionals were used in the construction process for a single PP. This requirement does not lead to a significant degradation of the PP accuracy. In comparing results for various test sets with experiment and all electron calculations, it was found that the most important approximation on the whole remains the density functional approximation. The PP approximation is clearly less severe than the density functional approximation. The PP remains a significantly more severe approximation than the other numerical approximations and truncations inherent in the DMol (Ref. 3) all electron approach. The parametrization of the DSPP and its core corrections results in a small data set to be handled. Yet there is enough flexibility to assure that no significant improvements in accuracy could be obtained by a more extensive parametrization.

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