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LETTER TO THE EDITOR

Ab initio pseudopotentials from atom-in-jellium calculations

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Abstract. The well established procedure for the generation of *ab initio* pseudopotentials starts with the free atomic structure as a reference state. We propose the atom in jellium as a new reference state, which permits the generation of norm-conserving pseudopotentials based on scattering phase shifts. The use of this reference state eliminates some of the difficulties associated with the free-atom reference state. We demonstrate the method with an application to sodium atoms and dimers. The calculated equilibrium distance and binding energy agree very well with those of Batchelet, Hamann and Schlüter (BHS) potentials.

Pseudopotential (PP)-based electronic-structure calculations are widely used for accurate determination of a number of properties of solids. The advances in total-energy calculations and *ab initio* molecular dynamics have given impetus for large-scale electronic-structure calculations involving a few hundred atoms [1]. These methods, pioneered by Car and Parrinello [2] employ techniques such as simulated annealing and conjugate-gradient (CG) minimization and permit a large class of physical properties of the materials to be investigated from first principles. The key ingredient in all such calculations is reliable *ab initio* pseudopotentials. An excellent review of the modern techniques of electronic-structure calculations involving iterative diagonalization is due to Payne *et al* [3].

The role of good PPs, which act as an input to such calculations, need not be emphasized. During the past decade or so reliable determination of first-principle PPs has been possible due to the work of Hamann and co-workers [40]. These PPs are available in parameterized, easy-to-use form and have a number of desirable properties [5]. Apart from being *ab initio* they are norm-conserving, leading to good transferability. Moreover, real and pseudo-wavefunction, their logarithmic derivative and first energy derivative agree beyond a chosen radius. They include relativistic effects.

All the first-principle PPs reported so far share a common property, namely they are all derived from the reference-state calculation of the appropriate free-atom configuration. However, as pointed out by Hamann [6], there are a number of difficulties, which prompted him to introduce generalized norm-conserving potentials. For example, it is necessary to have non-local PPs for angular momentum l going up to three or four and the states with these angular momenta need not be amongst the ground-state atomic configuration. Usually such potentials are calculated by using additional ionized atomic configurations. Firstly, this is inconvenient and, secondly, it can lead to errors. It is not possible [6] to obtain PPs for rare-gas atoms where the interest is only in their repulsive interactions, which may be required for a class of applications, e.g. rare-gas-surface interaction. It has also been pointed out that for atoms such as Cs and Ba the resulting potentials are too strong.

In the present work we propose a method that starts with a different reference system and offers a natural remedy for the above-noted problems. The basic idea is to generate PPs

via scattering phase shifts, i.e. to generate the pseudopotentials that will reproduce scattering phase shifts for an appropriately chosen reference state. The question is what would be the proper reference system, which is simple enough to permit the reference-system calculation and yet capture the essential physics, maintaining the required features of the existing PPs. It is also desirable to be able to generate PPs as soft as possible, especially for 3d atoms. We propose to use, as a reference system, an atom embedded in jellium of appropriate density and demonstrate that Hamann, Schlüter and Chiang (HSC) procedure yields reasonably good PPs for a class of systems. Thus, we generate the PPs that reproduce scattering phase shifts of the conduction electrons calculated using the atom-in-jellium model. The procedure can be naturally applied for the case of 3d atoms as well, where the phase shift for the $l = 2$ component shows resonance. It is also possible to generate, with equal ease, the PPs for rare-gas atoms by embedding them in jellium of suitable density. In this work we demonstrate the feasibility of this procedure for the simple metal atom sodium.

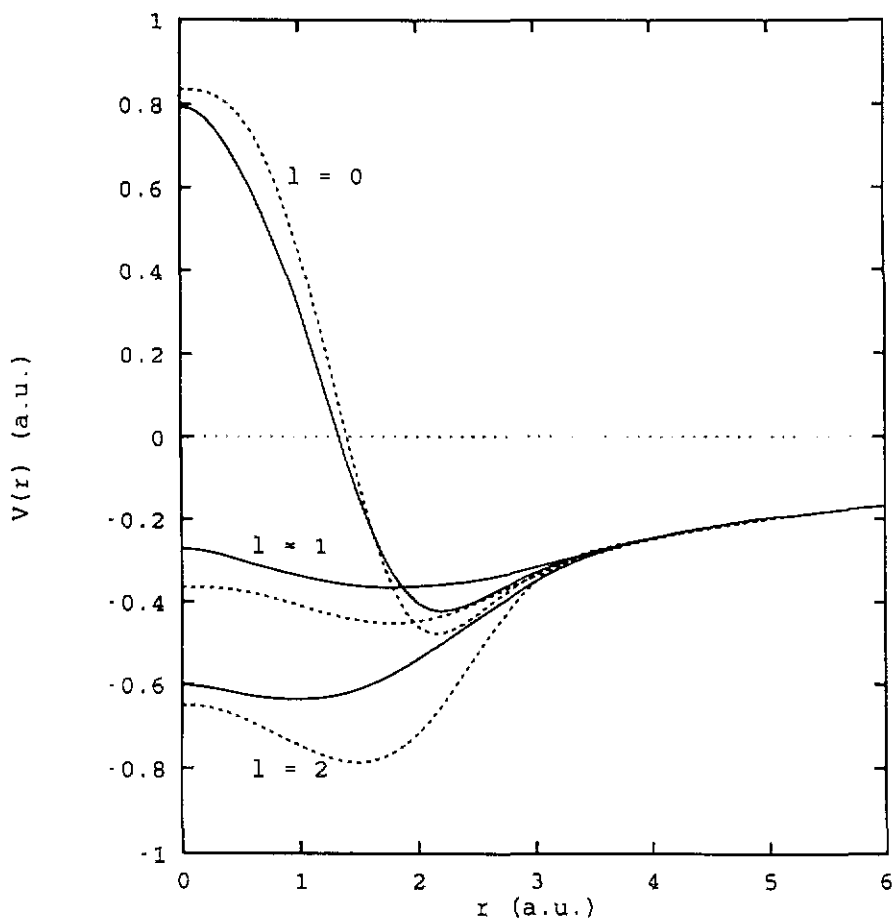


Figure 1. Ion core pseudopotentials for sodium for $l = 0, 1$ and 2 ; full curves, present potentials; dotted curves, BHS potentials.

The atom-in-jellium model has been extensively used for calculating a number of properties [7-10] such as core level and Auger binding energies, chemisorption, optical

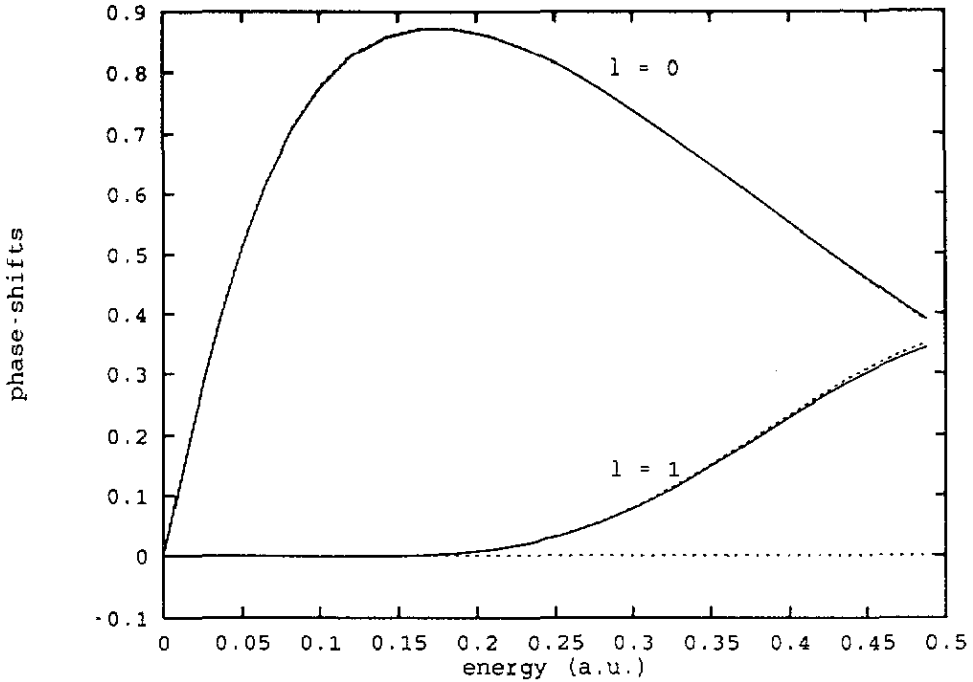


Figure 2. A comparison of pseudopotential phase shifts (full curve) with all-electron pseudopotential phase shifts (dotted curve).

properties of pure metals, interatomic forces etc. For the sake of completeness we give a brief discussion of the model. Consider a point charge Z immersed in jellium of density n_0 along with Z electrons. The central problem is to calculate the response of the electrons to this charge. This system has bound core states and positive energy-scattering or conduction-electron band states up to the Fermi energy ϵ_F . The full self-consistent all-electron calculation performed within the framework of density-functional theory yields all-electron scattering wavefunctions and phase shifts over the entire range of band energy (up to ϵ_F) and for angular momenta up to $l = 8$ or so. For the case of simple metals, the choice of the host jellium density is the metallic density, while for neon, argon or transition metals, a convenient choice may be around $r_s = 2$. At this density, the transition-metal atoms show resonance for $l = 2$ and clearly it is essential to reproduce this resonance by generated PPs. It may be noted that the core states in our reference system are not atomic but are relaxed ones, due to the surrounding jellium solid, which is a desirable feature while generating PPs appropriate for extended systems.

The density-functional equations in atomic units, to be solved self-consistently, are

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (1)$$

where the effective potential $V_{\text{eff}}(\mathbf{r})$ is given by

$$V_{\text{eff}}(\mathbf{r}) = \phi(\mathbf{r}) + \delta E_{\text{xc}}[\rho(\mathbf{r})]/\delta\rho(\mathbf{r}) \quad (2)$$

and the total electronic charge density is

$$\rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2 \quad (3)$$

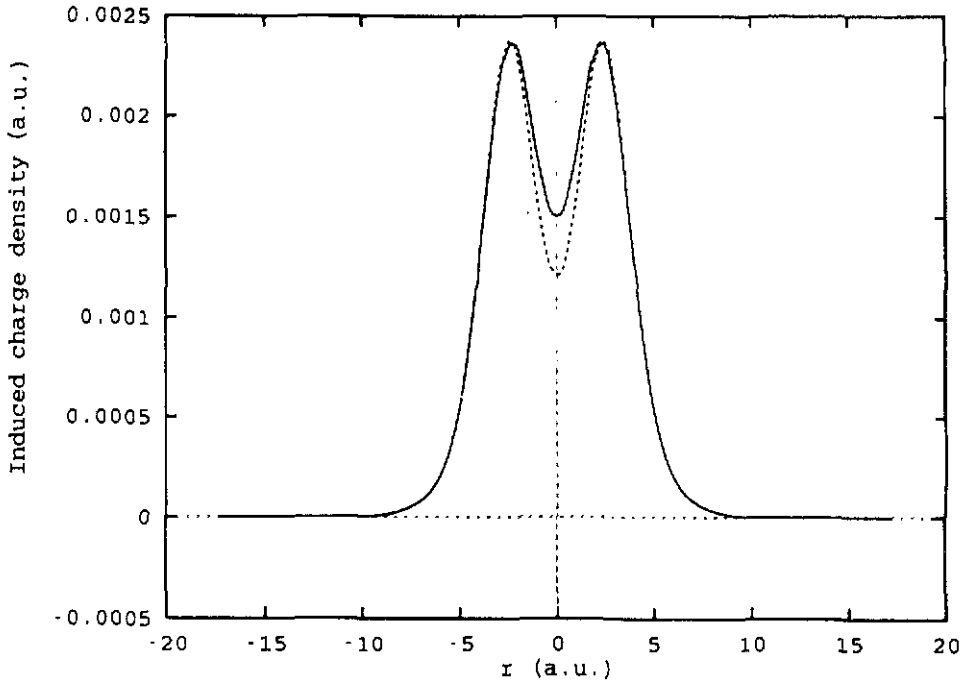


Figure 3. Pseudocharge densities for the sodium atom: full curve, present potentials; dotted curve, BHS potentials.

where $\phi(\mathbf{r})$ is the total electrostatic potential of the system and ϵ_i , $\psi_i(\mathbf{r})$ and n_i are respectively the eigenvalue, eigenfunction and the occupancy of the i th state. The second term in equation (2) is the exchange correlation potential. The sum in equation (3) runs over all occupied states including the conduction electron state.

Our interest is in the induced charge density $\delta\rho(\mathbf{r})$ around an ion

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum_i n_i |\psi_{bi}(\mathbf{r})|^2 - n_0 \quad (4)$$

where n_0 is the jellium density and $\psi_{bi}(\mathbf{r})$ is the bound electron wavefunction. The charge neutrality condition is

$$\int d^3r \delta n(\mathbf{r}) = Z\nu \quad (5)$$

$Z\nu$ being the valency of the atom. In our calculations the Friedel sum rule

$$Z\nu = \frac{2}{\pi} \sum_l (2l+1) \delta_l(\epsilon_F) \quad (6)$$

is satisfied to within less than 1% where $\delta_l(\epsilon_F)$ is the phase shift for the l th partial wave at the Fermi level.

At the end of the reference calculation, we have the all-electron phase shifts, the scattering-state wavefunction and the effective potential V_{eff} . The HSC procedure is now followed.

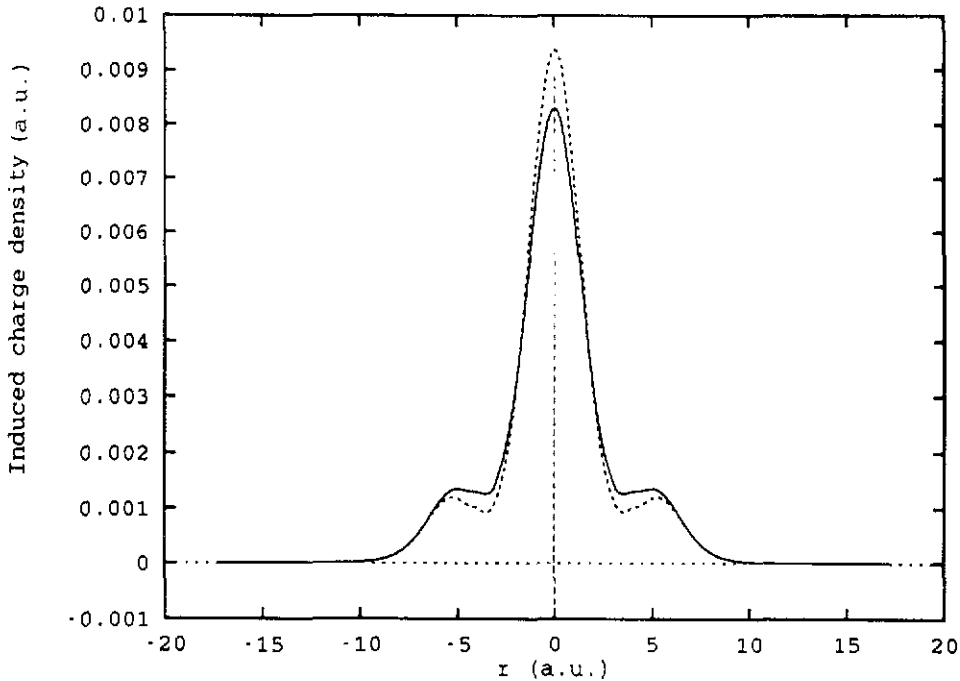


Figure 4. Pseudocharge densities for the sodium dimer: full curve, present potentials; dotted curve, BHS potentials.

Thus the next step is to construct a first-step PP $V_l^1(r)$ as

$$V_l^1(r) = V_{\text{eff}}(r)[1 - f(r/r_{cl})] + C_l f(r/r_{cl}) \quad (7)$$

where $f(r/r_{cl})$ is a smooth cut-off function. The constant C_l is now adjusted so that the phase shift calculated at the chosen energy, usually between zero and ϵ_F , and for a given value of l at the chosen radius is exactly identical to the full-potential phase shift. This is then followed by the norm-conserving step and unscreening to give the desired PPs. This procedure correctly reproduces the all-electron Friedel sum rule. In the present work we have chosen to match the phase shifts at energies $\frac{1}{2}\epsilon_F$ and, as will be shown later, the resulting pseudopotential reproduces the all-electron phase shifts over the entire range of band energies. In fact, this forms an excellent criterion for the choice of r_{cl} and the matching energy. It may be noted that for transition-metal atoms it is necessary to match $l = 2$ phase shifts to give the correct resonant behaviour.

As an application of this procedure we have generated the PPs for sodium. In all the calculations the Von Barth-Hedin exchange correlation potentials have been used. The phase shifts have been matched at $\frac{1}{2}\epsilon_F$ and $r_{cl} = 1.6, 2.1$ and 2.3 for $l = 0, 1$ and 2 respectively. The resulting potentials for $l = 0, 1$ and 2 along with Batchelet, Hamann and Schlüter (BHS) potentials [5] are shown in figure 1. In all cases the full curve corresponds to the present results and the dotted curve to BHS results. It can be seen that the two potentials are very similar, although our PPs for $l = 1$ and $l = 2$ are less deep.

How good are these PPs so far as the transferability is concerned? First, we show the phase shifts for the pseudopotential over the entire energy range $0-\epsilon_F$ along with full

potential phase shifts in figure 2 for $l = 0, 1$. The two curves are indistinguishable, indicating the quality of the potentials. We have also calculated the atomic structure for the isolated sodium atom using the plane-wave expansion in the large-unit-cell approach. The calculated charge densities for the present results and those obtained by an identical calculation using BHS potentials are shown in figure 3. As expected, the density agrees beyond $r = 2.1$. Our eigenvalue, though not identical with that of BHS, agrees to within 1%. The difference in the densities near the origin is clearly due to the differences in the PPs in the ion core region. The quality of our potentials is further tested by calculating the equilibrium distance for the sodium dimer using the large-unit-cell approach and CG minimization. The calculation is fully self-consistent, with an energy cut-off of 5.0 Ryd, requiring 8289 plane waves. An identical calculation has also been performed for BHS potentials. The calculated lattice constant and binding energy for the present potential are 5.74 au and 0.77 eV respectively. These results compare very well with those obtained by BHS PPs which are 5.68 au and 0.70 eV. The charge densities for both cases are shown in figure 4.

In conclusion, we have presented a method of generating *ab initio* pseudopotentials based on an atom-in-jellium reference calculation. Our results for sodium demonstrate that the resulting potentials are of comparable quality with the existing ones, that they are norm-conserving and that they have the same virtues as BHS potentials. Further, the use of the atom-in-jellium reference state avoids taking recourse to either excited-state configurations or positive-energy wavefunction calculations as done in [6]. Although we have presented results only for sodium, we have generated the PPs for copper, argon and neon. The detailed calculations for these systems will be presented elsewhere.

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