

Implementation of ultrasoft pseudopotentials in *ab initio* molecular dynamics

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A scheme for the construction of ultrasoft separable pseudopotentials recently proposed by Vanderbilt is tested in the context of Car-Parrinello *ab initio* molecular-dynamics calculations on atoms and molecules. For the case of oxygen, the transferability of the pseudopotential is demonstrated by comparing the calculated properties of molecular O₂ and O₃ with those obtained from conventional approaches. Converged results are obtained using plane-wave-basis cutoffs of only ~25 Ry. Forces can be calculated efficiently, and a molecular-dynamics simulation of molecular vibration is demonstrated.

First-principles electronic-structure calculations based on norm-conserving pseudopotentials¹ and plane waves are a powerful tool to investigate the properties of materials. In particular, with the development of *ab initio* molecular-dynamics techniques,² it has become possible to study large and disordered systems, as well as finite temperature and dynamical properties. So far this approach has been applied mainly to *sp*-bonded systems characterized by relatively soft pseudopotentials. There is, however, considerable interest in applying the same technique to a more general class of systems including first-row and transition-metal elements, which exhibit a large degree of valence-electron localization. Since conventional pseudopotentials¹ require a prohibitively large number of plane waves to deal with such systems, several efforts have been recently made to develop optimally soft pseudopotentials^{3,4} or to combine augmented plane-wave (APW) ideas with *ab initio* molecular-dynamics techniques.^{5,6}

The new scheme proposed by Vanderbilt³ combines the conceptual simplicity of pseudopotential approaches with the very rapid plane-wave convergence typical of APW methods. In this paper we show that Vanderbilt pseudopotentials, which so far have been tested only in the context of spherically symmetric atomic calculations, can be conveniently incorporated in *ab initio* molecular dynamics codes for condensed-matter computations. Using atomic and molecular oxygen as a test system, we show that the new pseudopotentials have transferability properties as good as those of standard norm-conserving pseudopotentials,¹ but require a dramatically lower plane-wave basis cutoff. In addition, forces can be efficiently evaluated and Car-Parrinello molecular-dynamics simulations of the Born-Oppenheimer motion of the atoms can be performed with little overhead compared to conventional separable nonlocal pseudopotentials^{7,8} using the same plane-wave cutoff.

We begin by reviewing the pseudopotential scheme introduced by Vanderbilt³ in the context of the variational expression for the total energy of the electron system. In

conventional schemes, this takes the form

$$E_{\text{tot}} = \sum_{\alpha} \langle \psi_{\alpha} | T + V_{\text{NL}} | \psi_{\alpha} \rangle + \int d\mathbf{r} n_v(\mathbf{r}) V_{\text{loc}}^{\text{ion}}(\mathbf{r}) + E_{\text{HXC}}[n_v] \quad (1)$$

subject to the constraint that the ψ_{α} are orthonormal. Here T is the kinetic energy, $V_{\text{loc}}^{\text{ion}}$ and V_{NL} are the (unscreened) local and nonlocal contributions to the pseudopotential, E_{HXC} is the Hartree-exchange-correlation functional, and $n_v(\mathbf{r})$ is the valence-electron density constructed from the ψ_{α} . In order that the pseudo-Hamiltonian match the all-electron Hamiltonian outside the cutoff radius r_c , we must have $V_{\text{NL}}(\mathbf{r}, \mathbf{r}') = 0$ and $V_{\text{loc}}^{\text{ion}}(\mathbf{r}) = V_{\text{AE}}^{\text{ion}}(\mathbf{r})$ for all $|\mathbf{r}|$ or $|\mathbf{r}'| > r_c$. Virtually all pseudopotentials currently in use, including semilocal potentials such as those of Bachelet, Hamann, and Schlüter¹ and fully nonlocal ones such as those of Kleinman and Bylander,⁷ can be written in the above form.

Vanderbilt³ has pointed out that such a pseudopotential scheme can be generalized further if the orthonormality condition on the wave functions is replaced by the condition

$$\langle \psi_{\alpha} | S | \psi_{\beta} \rangle = \delta_{\alpha\beta} \quad (2)$$

and the usual formula for constructing the valence charge density is replaced by

$$n_v(\mathbf{r}) = \sum_{\alpha} \langle \psi_{\alpha} | K(\mathbf{r}) | \psi_{\alpha} \rangle. \quad (3)$$

In order that the pseudosecular equation match the all-electron one outside r_c , we must have $S(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}')$ and $K(\mathbf{r}; \mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'')$ for all $|\mathbf{r}|$, $|\mathbf{r}'|$, or $|\mathbf{r}''| > r_c$. Furthermore, the condition that the integral of $n_v(\mathbf{r})$ should result in the correct total valence charge implies that S and K are related by

$$\int d\mathbf{r} K(\mathbf{r}; \mathbf{r}', \mathbf{r}'') = S(\mathbf{r}', \mathbf{r}''). \quad (4)$$

In this framework, the pseudopotential is uniquely described by specifying the functions $V_{\text{loc}}^{\text{ion}}(\mathbf{r})$, $V_{\text{NL}}(\mathbf{r}, \mathbf{r}')$,

and $K(\mathbf{r}; \mathbf{r}', \mathbf{r}'')$ inside the sphere of radius r_c . The minimization of Eq. (1) subject to the constraint (2) leads to a secular equation of the form $H|\psi_a\rangle = \epsilon_a S|\psi_a\rangle$, where the screened Hamiltonian H is to be determined self-consistently.

It is useful to introduce a set of orthonormal basis functions $\beta_i(\mathbf{r})$ which vanish outside r_c and which span the space $r < r_c$. Then

$$V_{\text{NL}} = \sum_{i,j} D_{ij}^{(0)} |\beta_i\rangle \langle \beta_j|, \quad (5)$$

$$K(\mathbf{r}) = |\mathbf{r}\rangle \langle \mathbf{r}| + \sum_{i,j} Q_{ij}(\mathbf{r}) |\beta_i\rangle \langle \beta_j|, \quad (6)$$

$$S = 1 + \sum_{i,j} Q_{ij} |\beta_i\rangle \langle \beta_j|, \quad (7)$$

where $Q_{ij} = \int d\mathbf{r} Q_{ij}(\mathbf{r})$ [note $Q_{ij}(\mathbf{r})$ vanishes for $r > r_c$]. The index i should be regarded as a composite index $i \rightarrow (I\tau lm)$, where I specifies site and atomic species while τ and lm are radial and angular quantum numbers, respectively. Both $D_{ij}^{(0)}$ and $Q_{ij}(\mathbf{r})$ are diagonal in the site index I . For a given site $D_{ij}^{(0)} \rightarrow D_{\tau\tau' l' l'' m m'}^{(0)}$ and $Q_{ij}(\mathbf{r}) \rightarrow Q_{\tau\tau' l' l'' m m'}(\mathbf{r}) \rightarrow Q_{\tau\tau' l' l'' LM}(\mathbf{r})$, where the latter quantity is defined by the usual angular momentum addition rules. Finally, imposing spherical symmetry of the pseudopotential results in $D_{ij}^{(0)} \rightarrow D_{\tau\tau'}^{(0)}$ and $Q_{ij}(\mathbf{r}) \rightarrow Q_{\tau\tau' l' l''}(r)$ (and also $Q_{ij} \rightarrow Q_{\tau\tau' l}$). Thus, the quantities $D_{\tau\tau'}^{(0)}$ and $Q_{\tau\tau' l' l''}(r)$, together with the local potential $V_{\text{loc}}^{\text{ion}}(r)$ and the basis functions $\beta_n(r)$, suffice to define the pseudopotential completely.

A scheme of this type will be most efficient if the pseudopotential is separable (i.e., constructed in such a way that the sums are truncated to a few τl pairs). Vanderbilt³ has proposed an algorithm for constructing such separable pseudopotentials, in which: (i) the eigenvalues and eigenfunctions (outside r_c) are reproduced exactly by construction for a reference configuration; (ii) the pseudopotential and all-electron logarithmic derivatives (in the reference configuration) are made to match with arbitrary accuracy over the energy range of occupied states; and (iii) the pseudo wave functions are smooth inside r_c , and therefore require a very modest plane-wave cutoff. We have developed a version of the Car-Parrinello *ab initio* molecular-dynamics codes which implements the Vanderbilt pseudopotentials, and have used it to test the transferability and efficacy of the new potentials in the molecular environment.⁹ (In fact, the new version of the codes could equally be applied to any separable potential of the general form given above, so that possible improvements to the specific algorithm proposed by Vanderbilt could readily be tested.)

We have generated several versions of the Vanderbilt potentials for oxygen, with different cutoff radii and different numbers of radial functions $\beta_{\tau l}$, in order to test how the transferability and plane-wave convergence properties depend on these parameters. In Table I, the transferability properties in the atomic environment are summarized for these potentials by reporting two quantities: $\epsilon_{ps}(sp^5)$ is the eigenvalue difference $\epsilon_p - \epsilon_s$ in the sp^5 configuration, and $\epsilon_p(s^2p^3)$ is the p eigenvalue in the s^2p^3 configuration. (The former is found to be a good predictor of eigenvalues and promotion energies for neutral ex-

TABLE I. Transferability tests of Vanderbilt pseudopotential in atomic environment. Results are also given for all-electron and exact frozen-core calculations. Unless otherwise noted, the pseudopotential was constructed in the ground-state configuration, without partial core correction, with two reference energies (τ values) for each of s and p , and $r_0 = 0.6$ a.u. and $r_c^{\text{loc}} = 1.0$ a.u. in the notation of Ref. 3.

Type	r_c (a.u.)	$\epsilon_{ps}(sp^5)$ (Ry)	$\epsilon_p(s^2p^3)$ (Ry)
All electron	. . .	1.0702	1.8077
Frozen core	. . .	1.0702	1.8077
Potential 1 ^a	1.2	1.0703	1.8078
Potential 2	1.2	1.0692	1.8075
Potential 3	1.5	1.0693	1.8084
Potential 4	1.8	1.0693	1.8094
Potential 5 ^b	1.2	1.0692	1.8123
Potential 6 ^b	1.5	1.0693	1.8268

^aConstructed with partial core correction and $r_0 = 0$.

^bConstructed with only one reference energy for each of s and p .

cited states $s^{2-x}p^{4+x}$, while the latter is a good predictor for ionic excitations s^2p^{4-x} .)

The first three lines of Table I show that freezing the $1s$ core is an excellent approximation, and that it is possible to construct a pseudopotential (potential 1) with cutoff radius 1.2 a.u. which gives essentially perfect transferability. Here the functions Q_{ij} have not been pseudized, and the “partial core correction” of Louie, Froyen, and Cohen¹⁰ has been included. If instead the Q_{ij} are pseudized at $r_0 = 0.6$ a.u. and the partial core correction is omitted (potential 2), the agreement is still excellent.¹¹ Therefore, we have chosen to incorporate these approximations into all oxygen potentials subsequently generated. Next, note that the deterioration of the transferability as the cutoff radius r_c is increased (potentials 3 and 4) is very modest. Based on these atomic tests, we would judge any of these potentials to be of comparable high quality to a typical conventional pseudopotential [e.g., Bachelet-Hamann-Schlüter (BHS) pseudopotential¹¹ with much smaller cutoff radius. Finally, we did try generating pseudopotentials (5 and 6) with only one reference energy for each of s and p , but it can be seen that the transferability deteriorates sharply for $r_c > 1.2$ a.u. (Most of the deterioration comes from the p part.) We have therefore chosen to focus on potentials 2, 3, and 4 as candidates for use in solid-state and molecular calculations.

We have checked the convergence of these three potentials as a function of plane-wave cutoff, for the case of the free oxygen atom in a cubic supercell (10 a.u. on a side). Rappe *et al.*⁴ have emphasized that this should be a good predictor of convergence in the solid-state environment. The results are shown in Fig. 1, along with corresponding results for a conventional BHS pseudopotential.¹ It is immediately evident that the new potentials are converged by about 20–30 Ry, depending on the r_c used, while the conventional potential requires a cutoff larger than 100 Ry.

Returning now to the question of transferability, we note that the atomic tests described so far only involve environmental changes which do not disturb the spherical

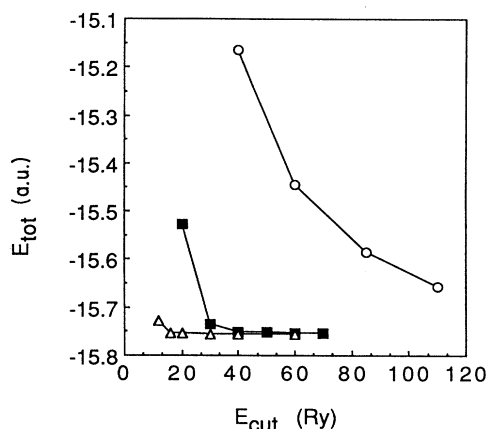


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

symmetry. A much more stringent test is the O_2 dimer, in which the atomic environment is highly asymmetrical and a strong covalent bond has been formed. Using the same cubic supercell discussed above, we have carried out calculations of the eigenvalues and binding energy of the dimer as a function of interatomic distance. The equilibrium bond length d , vibrational frequency ω , and binding energy E_{bind} were extracted by fitting to a series of calculations of total energy versus d . The results are summarized in Table II, where the corresponding results obtained from a BHS pseudopotential¹ are given for comparison. (We have avoided making a direct comparison with results from local-spin-density approximation calculations¹²⁻¹⁴ and with experiment¹⁵ because spin polarization has not been included in the present calculations.) First, we note that the pseudopotentials with cutoff radius 1.2, 1.5, and 1.8 a.u. show convergence by 30, 25,

TABLE II. Transferability and convergence tests of Vanderbilt (V) pseudopotential in molecular environment. Equilibrium bond length d , vibrational frequency ω (in harmonic approximation), and binding energy E_{bind} are given. Corresponding results obtained using a Bachelet-Hamann-Schlüter (BHS) pseudopotential are provided for comparison.

Approach	E_{cut} (Ry)	d (a.u.)	ω (cm^{-1})	E_{bind} (eV)
V ($r_c = 1.8$ a.u.)	20	2.41	1840	9.7
	25	2.40	1780	9.8
V ($r_c = 1.5$ a.u.)	20	2.29	1760	10.0
	25	2.30	1760	10.1
	30	2.30	1800	10.1
V ($r_c = 1.2$ a.u.)	20	2.49	1130	9.1
	30	2.32	1650	9.8
	50	2.30	1610	9.8
BHS ^a	40	2.40	1170	9.0
	85	2.30	1490	9.6
	125	2.29	1660	9.8

^aReference 1.

and 20 Ry, respectively. For the BHS pseudopotential, a cutoff of more than 85 Ry is required to obtain comparable convergence. Thus, the convergence of each pseudopotential is much faster than that of BHS. Next, to compare transferability, we concentrate just on the converged results for each version of the pseudopotential. The pseudopotentials with cutoff radius 1.2, 1.5, and 1.8 a.u. show excellent, good, and fair transferability, respectively. These results demonstrate that chemically accurate results can be obtained with the Vanderbilt scheme, even though the oxygen $2p$ radial wave-function maximum is drastically reduced and shifted in radius.

So far, we have reported only static total-energy calculations. However, the present scheme also allows forces on the atoms to be calculated efficiently and without approximation. When evaluating the forces one must be careful to include the contribution from the site dependence of the operator S in the constraint (2). Then the equations of motion given by Car and Parrinello² can be used to update simultaneously atomic positions and electronic wave functions. Under appropriate conditions, the fictitious Car-Parrinello dynamics reproduces very closely adiabatic Born-Oppenheimer atomic motion. For example, by performing a Car-Parrinello molecular-dynamics (MD) simulation of a vibrating oxygen dimer, we obtain the oscillatory motion plotted in Fig. 2. The system was allowed to evolve freely from an initial configuration in which the atoms were slightly displaced from equilibrium and the electrons were in the ground state. We used a pseudopotential with $r_c = 1.5$ a.u., a plane-wave cutoff $E_{\text{cut}} = 25$ Ry, a Verlet time step $\Delta t = 3.6$ a.u. (0.09 fs), and a fictitious electron mass $\mu = 400$ a.u. As we can see, the vibration repeats harmonically for several periods with no apparent damping or change in frequency. No subsequent electronic minimization was necessary to keep the system close to the Born-Oppenheimer surface. The period of vibration, as obtained from the *ab initio* MD simulation, is 19.21 fs (frequency 1737 cm^{-1}), to be compared with 19.11 fs (1746 cm^{-1}) obtained from the static total-energy calculations. (To account for anharmonic effects, the latter value was obtained from a MD simulation using the fitted potential-energy surface.) This kind of accuracy is typical of *ab initio* MD simulations when using conventional pseudopotentials.² Moreover, we find

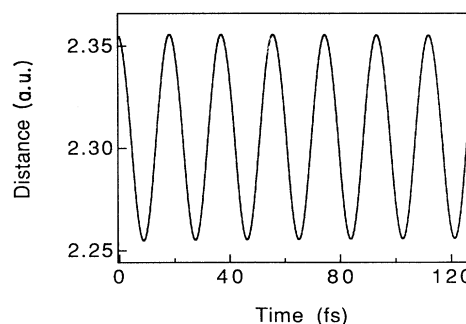


FIG. 2. Bond length of O_2 molecule vs time from *ab initio* molecular-dynamics simulation using $r_c = 1.5$ a.u. and $E_{\text{cut}} = 25$ Ry.

that the computational overhead required for the Vanderbilt scheme (compared to a standard separable pseudopotential⁷ at the same plane-wave cutoff) is modest, and arises mainly from the modified orthonormality condition (2) and from the need for two atomic reference energies for oxygen.

As a final test, we have performed calculations of the low-lying singlet states of the ozone (O_3) molecule. From previous calculations¹⁶ we know that in this molecule there are two important low-energy singlet states, corresponding to the cyclic (D_{3h}) and to the symmetric bent (C_{2v}) forms, the latter being the ground-state geometry. In these calculations we used two different pseudopotentials, one with $r_c = 1.5$ a.u. and the other with $r_c = 1.2$ a.u. Fully converged results were obtained with a cutoff of 25 Ry in the first case and 36 Ry in the second one. We summarize our results in Table III, where we also report the available experimental data¹⁷ and the results of a previous frozen-core local-density calculation using the linear muffin-tin orbital (LMTO) approach.¹⁶ The agreement with experiment and with a previous calculation is again very good. Note that in this case, essentially perfect convergence is already achieved with $r_c = 1.5$ a.u. The main reason to keep r_c small is to avoid significant core overlap; in this respect the oxygen dimer ($d \sim 2.3$ a.u.) is a rather extreme case, while the ozone molecule represents a slightly improved situation.

In conclusion, we have demonstrated the transferability of Vanderbilt pseudopotentials in the context of plane-

TABLE III. Bond lengths d and angles θ of O_3 in the bent (C_{2v}) and cyclic (D_{3h}) forms, obtained from Vanderbilt pseudopotentials (V) and previous theory and experiment. ΔE is the total-energy difference between cyclic and bent forms.

Approach	$d(C_{2v})$ (a.u.)	$\theta(C_{2v})$	$d(D_{3h})$ (a.u.)	ΔE (eV)
V ($r_c = 1.5$ a.u.)	2.38	117	2.66	1.3
V ($r_c = 1.2$ a.u.)	2.39	118	2.70	1.4
LMTO ^a	2.44	118	2.76	1.4
Expt. ^b	2.40	117

^aReference 16.

^bReference 17.

wave calculations on small oxygen molecules. We expect a similar behavior to occur also for other systems and for different condensed-matter environments. This scheme should allow *ab initio* molecular-dynamics simulations to be performed for a much wider class of systems than has been possible so far.

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