# 12 SCIENTIFIC HIGHLIGHT OF THE MONTH

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**FOREWORD**

The following paper from about 1994 is being published in Psi-k Newsletter because Physical Review has twice refused to do so, for reasons that are frankly unacceptable, in spite of meeting all the objections of the first round of refereeing.

Anyway it is not unsuitable for Psi-k Newsletter because some people still use norm-conserving pseudopotentials for a wide range of applications, and anyway the idea of the $Q_c$ tuning is now also being used elsewhere. Also these pseudopotentials are very good, the extra 'tuning' degree of freedom allowing one to match the logarithmic derivative as closely as possible, and to soften the energy cut-off for the plane waves, or to fit to some other empirical quantity such as a lattice constant. They are considerably softer than some pseudopotentials that are widely used, without loss of accuracy.

The paper is also being put on the e-Print archive server (http://arxiv.org/), and the code is freely available (see website http://boson4.phys.tku.edu.tw/qc/).

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# Kinetic energy tuning for optimising pseudopotentials and projector reduction

M.-H. Lee[a,b], J.-S. Lin[a,c], M.C. Payne[a,d], V. Heine[a,d], V. Milman[a,d], S. Crampin[a,e]

[a] *Cavendish Laboratory, University of Cambridge, Madingley Road, CB3 0HE, UK*

[b] *Present address : Department of Physics, Tamkang Univeristy, Tamsui, Taipei 251, Taiwan*

[c] *Present address : Department of Chemistry, Tamkang University, Tamsui, Taipei 251, Taiwan*

[d] *Present address : Molecular Simulation Inc., 240/250 The Quorum, Barnwell Road Cambridge, CB5 8RE, UK*

[e] *Present address : School of Physics, University of Bath, Bath BA2 7AY, UK*

### Abstract

We have developed an improved scheme for generating optimised norm-conserving pseudopotentials which is more systematic and more flexible, with a better insight. The control parameter $Q_c$ connected with the kinetic energy of the pseudo wavefunction $\Psi_l(r)$ is used in a new way to tune the pseudopotential. The scheme uses only three constraints and three spherical Bessel functions in the expansion of $\Psi_l(r)$ inside the pseudising radius $r_c$, compared with four commonly used, which tends to give a somewhat softer pseudopotentials. The fidelity of the pseudopotential as seen in the logarithmic derivative can be improved in a simple and systematic way by tuning $Q_c$ while minimising the energy cutoff $E_{\text{cut}}$ necessary in solid state application. The scheme opens the way to tailor-making pseudopotentials for specific requirements useful for large scale *ab initio* calculations, including reducing the number of non-local projectors for speeding up the calculations.

# 1 Introduction

The present paper concerns a further improvement of earlier schemes for generating norm-conserving pseudopotentials [1, 2, 3]. Soft and accurate pseudopotentials are essential for state-of-the-art large scale *ab initio* simulations for solids using plane-wave basis sets. This is in the context of periodic superlattice calculations based on Density Functional Theory with Local Density Approximation (LDA) for exchange and correlation with possibly a Generalised Gradient Approximation (GGA). Here, a ”soft” pseudopotential means that a low energy cut-off, $E_{\text{cut}}$, can be used in the planewave expansion of the wavefunction, and the ”accuracy” of a pseudopotential can be measured by the agreement between the logarithmic derivatives of pseudo and true wavefunctions in a certain energy range, which is an equivalent characterisation of the scattering property of a pseudopotential in terms of the phase shifts of different incoming waves. We are here concerned with norm-conserving pseudopotentials, as distinct from the super-soft pseudopotentials of Vanderbilt [4] which are not norm-conserving. Although the latter are widely used, we believe there is still a role for norm-conserving pseudopotentials because of certain computational efficiences, e.g. optical properties and stress are easier to implement. In any case it appears that the idea of $Q_c$ tuning can also be applied with advantage to the super-soft pseudopotential [5]. Even with the accuracy and efficiency achieved by a Car-Parrinello type of algorithm [6, 7], the computational cost still requires as soft a pseudopotential as possible to make the largest calculations affordable.

While the advantage of the softness in a pseudopotential can not be over-emphasised, what is equally important is to have a flexible scheme to generate quickly and systematically a new pseudopotential appropriate to a new physical situation, such as short inter-atomic distances in some compounds or at ultra high pressures. Another example would be some structural energy difference where errors cancel, so that one can compromise on convergence properties. A further situation might be one where the energy range over which the logarithmic derivative of the pseudo wavefunction has to be accurate is unusually narrow or wide. Whereas one standard transferable pseudopotential for a given chemical element may be satisfactory for many purposes, this will not be so for some calculations. On the contrary, the flexibility of balancing the accuracy (logarithmic derivative) and the efficiency ($E_{\text{cut}}$) of a pseudopotential in its construction will be useful, because then computing effort will not be wasted in achieving unnecessary precision. This utility can not be replaced by simply using an insufficient $E_{\text{cut}}$ in exchange for a less accurate result because the quality of computed physical quantities falls very rapidly when decreasing $E_{\text{cut}}$ below some point which is essentially determined by the way the pseudopotential is generated. A flexible scheme is therefore to be welcomed if it allows one to regulate the degree of approximation in different parts of a pseudopotential, such as the logarithmic derivative, $E_{\mathrm{cut}}$ and a large pseudising radius ("cut-off" radius) $r_c$ to maximise the pseudopotential performance in a given problem without compromising the science. A great computational efficiency has been achieved in a few cases (eg. reference [8]) by what we call 'projector reduction'. A normal pseudopotential consist of a local potential operating on all angular momentum $(l, m)$ components of the pseudo wavefunction, plus a few non-local potentials operating on specific l components only. For a non-transition element such as carbon, the latter would normally be for $l = 0$ and 1, requiring $1 + 3 = 4$ specific projectors in the computations to pick out these components from the total pseudo wavefunction. However using the flexibility of $Q_c$ tuning, we have been able to generate pseudopotentials for some elements where the $l = 1$ component is sufficiently nearly the same as that for $l = 2$ so that it can be taken as the local potential part, thus requiring only one projector for $l = 0$. This is particularly advantagous with the real-space implementation of Kleinman-Bylander form [9] for the non-local part of the pseudopotential [10]. The large dynamic simulation of methanol dissociation in a zeolite [8] could not have been carried out at that time without such projector reduction for carbon and oxygen. In the case of Cu and transition elements, we can achieve a pseudopotential with projectors for $l = 2$ only.

In order to generate a new pseudopotential efficiently, it is a great help to understand how changes in the input parameters affect the pseudopotential that results. Such understanding also helps one to avoid an unrealistic choice of parameters. We present in this chapter a robust way of constructing norm-conserving pseudopotentials which addresses those essential points mentioned above, namely acceptable accuracy, softness, flexibility and understanding, through further improvements to the well established "Optimised Pseudopotentials" approach. [1, 2, 3]. We regard our method as an alternative to the very popular schemes proposed by Troullier and Martins [11], by Vanderbilt [4], and by Blöchl [12]. These schemes all aim to improve the softness and/or the accuracy of pseudopotentials.

Before we describe the technical details of our current scheme, it is necessary to outline previous optimisation methods. The "Optimised Pseudopotentials" proposed by Rappe, Rabe, Kaxiras and Joannopoulos (RRKJ) [1, 2] are recognised as very soft norm-conserving pseudopotentials. Their scheme is very suitable for transition metals and first-row elements which we are interested in and which usually need higher $E_{\mathrm{cut}}$ than other elements due to their very localised $3d$ (or $4d$) or $2p$ valence electrons. Based on the RRKJ idea, a modified strategy of generating optimised pseudopotentials was suggested by Lin, Qteish, Payne and Heine (LQPH) [3] in order to simplify the numerical procedure. Although using different options and procedures, the basic formulations in LQPH and the current work are the same as those in the original RRKJ. In all these schemes the pseudo wavefunction $\Psi_l(r)$ of angular momentum $l$ is generated first, and then the pseudopotential $V_l(r)$ is derived from it by inverting the Schrödinger equation [13]. The $\Psi_l(r)$ is expressed in terms of some specially chosen spherical Bessel functions as follows :

$$\Psi_l(r) = \sum_{i=1}^{n} \alpha_i \; j_l(q_i r) \quad \text{for} \quad 0 < \mathrm{r} < \mathrm{r_c}, \quad \text{with} \quad \frac{\mathrm{j_l}'(\mathrm{q_i r_c})}{\mathrm{j_l(q_i r_c)}} = \frac{\phi_\mathrm{l}'(\mathrm{r_c})}{\phi_\mathrm{l}(\mathrm{r_c})}$$

$$\Psi_l(r) = \phi_l(r) \quad \mathrm{forr} \geq \mathrm{r_c} \tag{1.1}$$

in which the $j_l(q_i r)$ are spherical Bessel functions with $(i-1)$ zeros for $r < r_c$, and $j_l'(q_i r)$ their first derivative with respect to $r$. The $\phi_l(r)$ is the proper all-electron atomic wavefunction and $\phi_l'(r)$ its first derivative. Since we start with $\phi_l(r_c)$ when generating a new pseudopotential, all the $q_i$ are fixed once the $r_c$ is chosen. The portion of the kinetic energy of the pseudo wavefunction due to the $q > Q_c$ part of its Fourier components is denoted by $\Delta E_k$ (in atomic-Rydberg unit) :

$$\Delta E_k(\alpha_1, \alpha_2, ..., \alpha_n, Q_c) \ = \int_{Q_c}^{\infty} d^3q \ q^2 |\Psi_l(q)|^2 \tag{1.2$a$}$$

$$= \ - \int_{0}^{\infty} d^3r \ \Psi_l^*(r) \ \nabla^2 \Psi_l(r) \ - \ \int_{0}^{Q_c} d^3q \ q^2 |\Psi_l(q)|^2 \tag{1.2$b$}$$

in which the $\Psi_l(q)$ is the Fourier transform of the $\Psi_l(r)$. The central idea for optimising a pseudopotential was that for a given $Q_c$, the coefficients $\alpha_i$ of $\Psi_l(r)$ in (1.1) can be obtained by minimising $\Delta E_k$ in (1.2) with Lagrange multipliers constraining the normalisation and the continuity of the first and second derivatives of the pseudo wavefunction at $r_c$. Thus a smooth and norm-conserving pseudo wavefunction $\Psi_l(r)$ could be determined. Incidentally, the continuity of the pseudo wavefunction $\Psi_l(r)$ at $r_c$ is not imposed explicitly because the optimisation procedure results in this condition being fulfilled automatically. This can be understood from the definition of the $j_l(q_i r)$ in (1.1). We know that when the constrained minimisation is successful, one has $\Psi_l'(r_c) = \phi_l'(r_c)$ : therefore

$$\Psi_l(r_c) = \sum_{i=1}^{n} \alpha_i \ j_l(q_i r_c) = \sum_{i=1}^{n} \alpha_i \cdot \frac{\phi_l(r_c)}{\phi_l'(r_c)} \cdot \ j_l'(q_i r) = \Psi_l'(r_c) \cdot \frac{\phi_l(r_c)}{\phi_l'(r_c)} = \phi_l(r_c) \tag{1.3}$$

which gives the required continuity of $\Psi_l(r)$ from the continuity of $\Psi_l'(r_c)$ due to the special choice of expansion functions in (1.1). Although the mathematical scheme is essentially the same, there are some differences in the way the procedure is used by the previous authors and in the present work. In the RRKJ method, typically 10 or more spherical Bessel function terms in (1.1) were used, with $Q_c$ being varied iteratively such that the $\Delta E_k$ is minimised to a pre-chosen tolerance, say 1 $m$Ryd. It appears that using $Q_c$ in that way has the advantage of controlling the quality of the total energy convergence with respect to the energy cut-off used in the calculations. In the LQPH method, the number of spherical Bessel function terms was fixed to be four so that there are four $\alpha_i$ coefficients for the $\Psi_l(r)$ to be determined, making the number of free parameters equal to the number of constraints, namely norm-conservation, continuity of the first and second derivatives of $\Psi_l(r)$ at $r_c$, and minimisation of $\Delta E_k$. Efficient numerical routines exist for such a problem, and the reasonably small number (four) of terms in $\Psi_l(r)$ helps to stabilise the numerical procedure. In addition to using just four spherical Bessel function terms in $\Psi_l(r)$, the LQPH method always sets $Q_c$ equal to the largest $q_n$ , i.e. $q_4$ , which avoided the variation of $Q_c$ and therefore made the numerical procedure significantly simpler than that of RRKJ.

We recognise the success of the above mentioned schemes, but the consequences of some of their detailed assumptions, such as the value of $Q_c$, the number of terms and the choice of constraints, were not fully clear to us. In particular, the role of $Q_c$ in optimising pseudopotentials attracted our attention. From the definition in (1.2), $Q_c$ can be regarded as a kinetic energy filter controlling the constrained minimisation of the kinetic energy of $\Psi_l$ in the range $q > Q_c$. If the minimisation is effective, the resulting $k$-space pseudo wavefunction $\Psi_l(q)$ will be restricted as far as possible to the range $0 < q < Q_c$, which will subsequently determine the analogous behaviour of the pseudopotential $V_l^{ps}(q)$ in $k$-space in solid state applications. A unique correspondence is therefore likely to exist between $Q_c$ and the pseudopotential in $k$-space $V_l^{ps}(q, Q_c)$, which of course also applies to $Q_c$ and $V_l^{ps}(r, Q_c)$ in $r$-space due to the duality of $r$ and $k$ spaces. Most importantly, the scattering property of such a pseudopotential should also depend on $Q_c$ in some simple manner because it is all in the characteristics of $V_l^{ps}(q, Q_c)$. In the current scheme we therefore vary $Q_c$ to control the phase shift, i.e. logarithmic derivative, as will be demonstrated in Section 2. We shall call this "$Q_c$ tuning" and it will be the crux of the present work. Additionally, from the argument above we expect the $Q_c$ to correspond roughly to $E_{\text{cut}}$. The $Q_c$ therefore controls both the scattering property and the energy convergence of the pseudopotential in our new optimisation scheme.

On investigating the choice of constraints, we realised that it is not necessary to impose strictly the continuity of $\Psi_l''(r)$ at $r_c$ because minimisation of $\Delta E_k$ already more or less constrains the higher derivatives of $\Psi_l(r)$ by reducing its high $q$ amplitude. Moreover, dropping unnecessary constraints means that a less restricted and more efficient minimisation can be performed. Thus not only can a softer pseudopotential be obtained but also the resulting pseudopotential will be more sensitive to the choice of $Q_c$, which enhances the controllability of the pseudopotential by $Q_c$. We have, in fact, tried applying the $Q_c$ tuning within the four-term/four-constraint framework, and found that both logarithmic derivative and the shape of the pseudopotential do not vary systematically with respect to $Q_c$, which is presumably due to the extra (unnecessary) constraint which somehow restricts the effect of $Q_c$ tuning.

However with the use of three terms and three constraints, we found that the logarithmic derivative and pseudopotential varied smoothly with $Q_c$ so that one can use $Q_c$ tuning efficiently. This is the main reason for preferring the three-term/three-constraint framework. Incidentally, keeping the number of terms and unknown coefficients in (1.1) equal to the number of constraints is very helpful in maintaining a stable numerical procedure, as found by LQPH. We can also see why the pseudopotential becomes somewhat softer. To a first approximation, $E_{\text{cut}} = Q_c^2$ Ryd. if $Q_c$ is in atomic units as will be assumed hereafter, and $Q_c$ is approximately the maximum $q_i$. Thus omitting the term $j_l(q_4 r)$ reduces $E_{\text{cut}}$, because $j_l(q_4 r)$ has the maximum number of nodes and hence the highest Fourier components of the $j_l(q_i r)$.

Incidentally, the small discontinuity in $V^{ps}(r)$ at $r_c$, corresponding to the discontinuity in the second derivative of the pseudo wave-function, does not destroy the energy convergence. At the $q$ relevant to $E_{\text{cut}}$, the $V^{ps}(q)$ is determined by the general shape of $V^{ps}(r)$, by the discontinuity in $V^{ps}(r)$ at $r_c$ given by the discontinuity in second derivative of the pseudo wave-function, and by the wiggles in $V^{ps}(r)$ at $r$ just less than $r_c$ which are seen clearly in Fig. 1 (c) for example. For a good $E_{\text{cut}}$, these need not individually be zero but it is sufficient that they more or less cancel giving a small total $V^{ps}(q)$ over a range of $q$. In addition the discontinuity may give some very small Fourier components extending to very high $q$, which can affect the absolute energy convergence of a calculation but which cancel in the calculation of any physical quantity.

To summarise: using a three-term expansion in (1.1) and three constraints gives a stable nu-

Fig.1.(a)

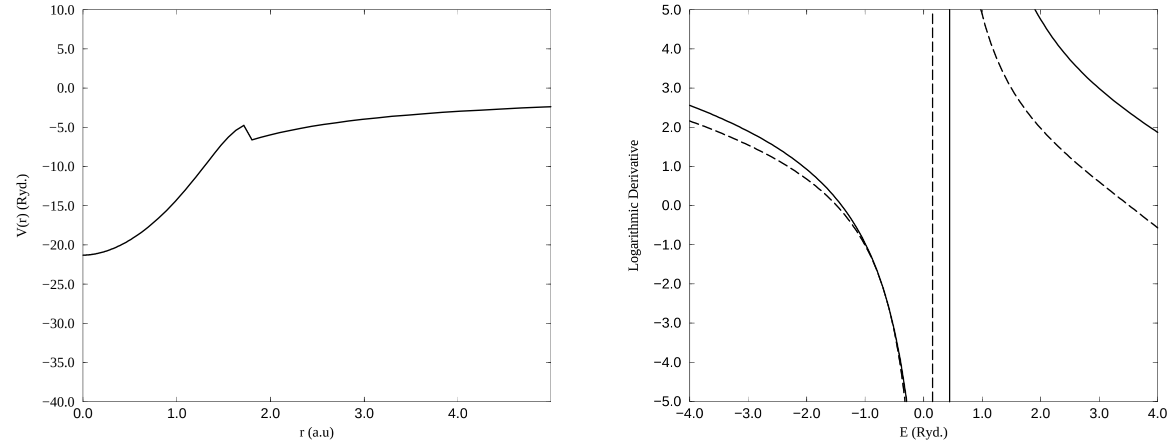

Fig.1.(b)

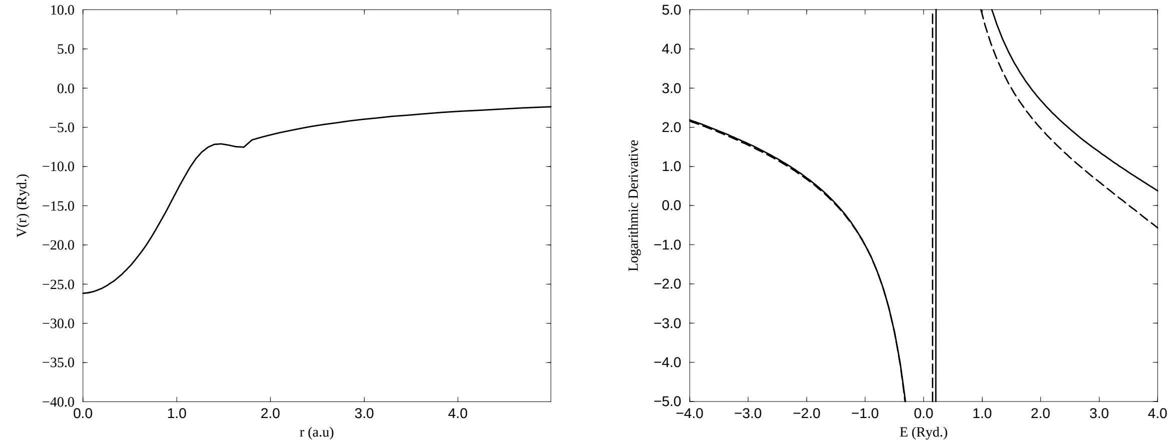

Fig.1.(c)

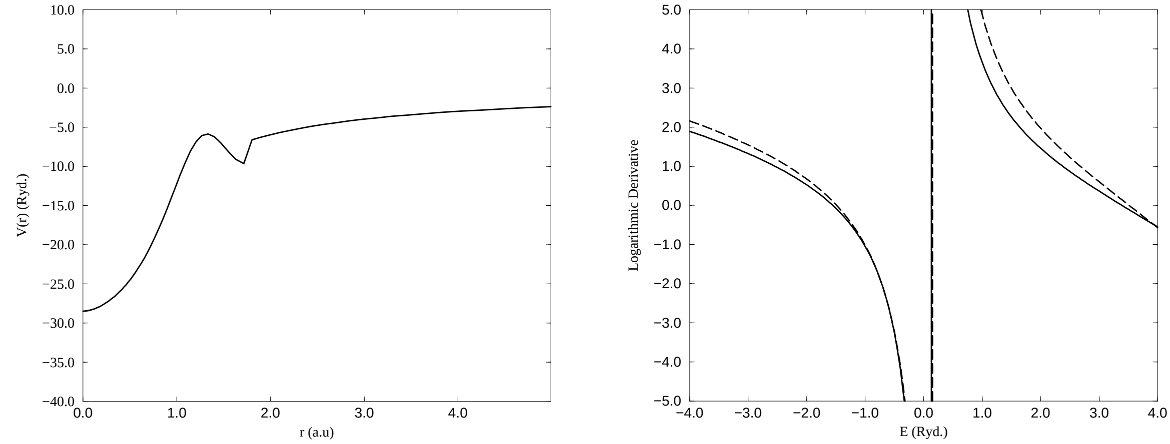

Figure 1: Oxygen $2p$ pseudopotential with $r_c$ =1.8 a.u. showing its variation with $Q_c$ . Left-hand-side panels, $V_{l=1}(r)$ : right-hand-side panels, logarithmic derivatives of the true potential (dashed line) and pseudopotential (solid line). (a) $Q_c/q_3 = 0.98$ (b) $Q_c/q_3 = 1.15$ (c) $Q_c/q_3 = 1.20$.

merical procedure allowing a good flexibility in the pseudo wavefunction. It combines well with tuning $Q_c$ to optimise the accuracy of the pseudopotential, which is the main purpose of the present work. The flexcibility can also be used to control the shape of the pseudopotential for different l and hence to reduce the number of projectors required in solid state applications. The limitation to three terms in (1.1) automatically gives a somewhat softer pseudopotential than previously. The effect of $Q_c$ tuning and relevant technical points are discussed in Section 2. In Section 3 some solid state tests of the pseudopotentials will be presented, which is followed by a discussion and conclusion as Section 4.

## 2 The $Q_c$ Tuning Method

To generate a pseudopotential in the current scheme, as in all *ab initio* pseudopotential generating procedures, an all-electron LDA or GGA atomic calculation is first performed to obtain all the atomic orbitals of a selected configuration : in the present work we just use the LDA. The procedure described in Section 1 is then implemented with three terms in (1.1) and the three constraints already discussed, while $Q_c$ remains as an adjustable input parameter. In Fig. 1 we demonstrate the effect of varying $Q_c$ in the current scheme on the oxygen $2p$ pseudopotential. Three different $Q_c$ were used to generate the corresponding pseudopotentials, and the logarithmic derivative was tested on these pseudopotentials. We can see that for a given atomic configuration and pseudising radius, there is a certain value of $Q_c$ which yields the best agreement with the logarithmic derivative, in this case that shown in Fig. 1(b). We note that the logarithmic derivative curve of the pseudo wavefunction for a larger and a smaller $Q_c$ deviate from the curve with the best possible $Q_c$ in opposite directions, as shown in Fig. 1(a) and Fig. 1(c). In Fig. 1 we also see that the shape of the pseudopotential changes with $Q_c$, which can be regarded as the reason why the scattering properties of the resulting pseudopotentials are different. The monotonic correspondence between the variation of (a) the $Q_c$, (b) the shape of the pseudopotential and (c) the logarithmic derivative of the pseudopotential is the most important feature in the current scheme. This feature enables us to establish a systematic procedure for updating $Q_c$ towards the best results judged by the following criterion. As mentioned in Section 1, $Q_c$ controls the softness of a pseudopotential as well as its accuracy because it affects both the $E_{\text{cut}}$ and the logarithmic derivative of the wavefunction. If transferability is a higher priority in a particular application, then $Q_c$ should be tuned to obtain the best match between the logarithmic derivatives of the pseudo and true wavefunctions. Depending on the application, one may require a good match over a wide range of energy for broad bands or only a narrower range in the case of narrow bands. If a satisfactory match can be obtained for a range of $Q_c$, then the smallest $Q_c$ should be used to achieve the lowest $E_{\text{cut}}$.

By removing the constraint on the second derivative of the wavefunction at $r_c$, we allow our pseudopotential to have a discontinuity there because the kinetic energy, which is proportional to $\Psi''(r)$, is discontinuous across $r_c$, and hence so is the potential. Although a large discontinuity in a pseudopotential can damage its scattering property, in the current scheme the best possible $Q_c$ is chosen to give the best fit of the logarithmic derivative, which thus guarantees that the discontinuity is harmless. This is also consistent with our observation that whenever the logarithmic derivative agreement is satisfactory, the discontinuity is always small. This can also be understood from the fact that in the current scheme the high $q$ components of the pseudo wavefunction are reduced as much as possible, both because they are expanded using the least possible number of spherical Bessel functions and also because of the minimising procedure imposed on $\Delta E_k$ in (1.2). The convergence of a practical calculation is not affected if a suitable $E_{\mathrm{cut}}$ is chosen, as already discussed in the previous section. Incidentally, it is generally the case that the $Q_c$ yielding the best fit to the logarithmic derivative of the true potential need not be the $Q_c$ that minimises the discontinuity of the pseudopotential, even though these two $Q_c$ are usually close. We regard the quality of scattering being optimised by the $Q_c$ as being more significant than the existence of the discontinuity.

The harmlessness of a small discontinuity is further confirmed by our experience that good agreement is obtained between the results of super-cell calculations using both $k$-space and $r$-space versions of the same pseudopotential expressed in Kleinman-Bylander form [9]. To convert the $k$-space pseudopotential to one in $r$-space we use the method of King-Smith et al. [10]. It will modify the original pseudopotential in a way that depends on $E_{\mathrm{cut}}$ in minimising the aliasing error of the Fast Fourier Transform in planewave supercell calculations. The discontinuity at $r_c$ in the original pseudopotential is smoothed out by the transformation. The fact that both the original and the transformed pseudopotentials gave almost identical results for the relaxation and energy of structures shows that the high $q$ feature at $r_c$ is irrelevant to the super-cell results when a reasonable $E_{\mathrm{cut}}$ is used.

## 3 Generation and Test of Some Pseudopotentials

Although the logarithmic derivative test gives useful indication about the quality of a pseudopotential, there is no precise criterion of how good the agreement should be for a particular physical application. Also the test is evaluated at a given $r$ outside the pseudising radius $r_c$, which does not give us the information whether the $r_c$ is small enough for the frozen core approximation to be valid for the given application. A solid state calculation is therefore always necessary for a serious test of a pseudopotential.

To test the pseudopotential generated by our current scheme, we have chosen some bulk properties of Cu metal because it is a popular case tested by other authors [1, 11]. We follow the RRKJ paper in using a slightly ionised Cu configuration $3d^{9.00}4s^{0.75}4p^{0.25}$ from which to generate the pseudopotential. After generating the pseudopotential for each $l$ as described in Section 2, it was converted to Kleinman-Bylander form with the $s$-potential chosen as the local potential. Two Cu pseudopotentials were prepared (Fig. 2), one with smaller $d$-core and the other a larger $d$-core, with $r_c(s,p,d) = (2.0, 2.0, 2.0)$ a.u. and $r_c(s,p,d) = (2.0, 2.0, 2, 4)$ a.u. respectively. The $Q_c$ for these two potentials are $Q_c(s,p,d) = (3.17, 4.66, 6.47)$ and $Q_c(s,p,d) = (3.17, 4.66, 5.17)$. In most cases, we found it useful to choose $q_3$ as the initial guess for $Q_c$ from which to start the tuning, so that it is convenient to express the final $Q_c$ in terms of the ratio $Q_c/q_3$. For the Cu pseudopotentials in this section, this becomes $Q_c/q_3(s,p,d) = (0.8, 1.0, 1.175)$ and $Q_c/q_3(s,p,d) = (0.8, 1.0, 1.2)$.

The Cu pseudopotential with the smaller $d$-pseudocore ($r_c = 2.0$ a.u.) allows our results to be compared directly with those of other popular schemes in the literature [1, 11], while we shall

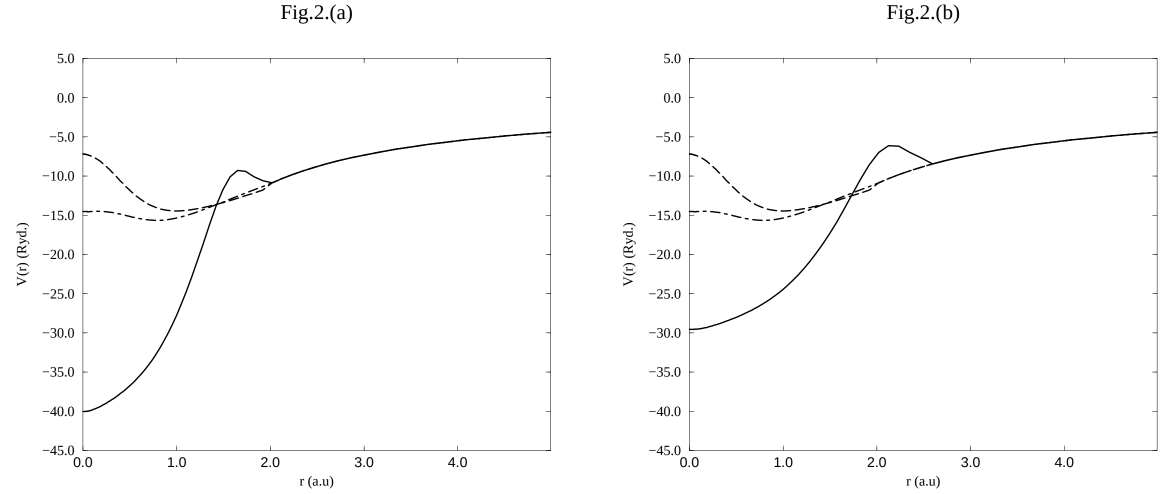
Fig.2.(a)

Fig.2.(b)

Figure 2: The $s, p, d$ pseudopotentials for Cu. (a) Small $r_c$=2.0 a.u. for $l = 0, 1, 2$. (b) $r_c$=2.0 a.u. for $l = 0, 1$ but larger $r_c$=2.4 a.u. for $l = 2$. ($s$: dashed line, $p$: dot-dashed line, $d$: solid line)

use the one with a big $d$-pseudocore to demonstrate the flexibility of using $Q_c$-tuning to generate a pseudopotential with a larger $r_c$. Although a pseudopotential with larger $r_c$ is always softer, it may not be accurate enough. In our current scheme we can tune the value of $Q_c$ so that we obtain a good logarithmic derivative even for such a large $r_c$.

For calculating the bulk properties of Cu metal, an $8 \times 8 \times 8$ Monkhorst-Pack $k$-point grid [14] was used for a simple-cubic unit cell containing four atoms. With such a coarse grid of $k$-points, a gaussian smearing of the occupation function at the Fermi level of $1eV$ was needed, and the energy was corrected appropriately [15]. In the case of the small $d$-core pseudopotential, the convergence test was done and the sudden drop of the total energy in a super-cell calculation was found to occur at 650 $eV$ where absolute convergence to about 0.1 $eV$ per atom is reached (Fig. 3). To justify the results obtained at $E_{\text{cut}} = 650\ eV$, a similar calculation was also performed at 1000 $eV$ where the total energy converged to within 0.01 $eV$ per atom, and the results for the bulk properties, as shown in Table 1, were found to be essentially the same. This is consistent with our experience that the $E_{\text{cut}}$ that gives the calculated total energy converged to around 0.1 $eV$ per atom is usually high enough for reliable solid state bulk properties. In the case of the pseudopotential with a large $d$-core, the convergence test was also done (Fig. 3) and we chose $E_{\text{cut}} = 500\ eV$ to run the simple bulk property tests which are shown as the third line in Table 1. Note that the valid comparison is with an exact all-electron calculation because we are testing the pseudising, not the accuracy of LDA, and we give the LAPW [16] results without knowing how closely it approximates to that. As one can see from the table, the overall result is satisfactory in comparison with experiment [17] and other computational methods.

We have already outlined in the Introduction the idea of "projector reduction", i.e. using $Q_c$ tuning to make the pseudopotentials for two angular momenta $i$ and $j$ sufficiently nearly the same that a common potential can be used for both. The latter then becomes the local

FIG.3

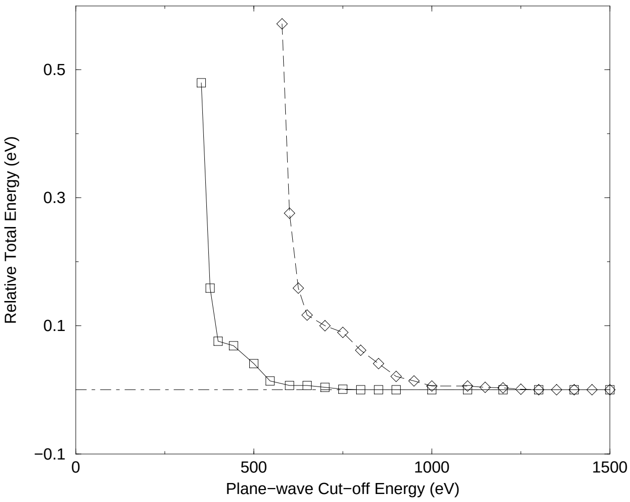

Figure 3: Convergence of total energy per atom of copper metal with respect to the cut-off energy for two pseudopotentials with $r_c$=2.5 a.u. (solid line) and $r_c$=2.0 a.u. (dashed line).

component $V_{\mathrm{L}}(r)$ of the atomic pseudopotential, leaving only one set of projection operators for the third angular momentum component. The elements B, C, N, O in the first row of the periodic table have only 1$s$ orbitals in the atomic core and hence both the $p$ ($l = 1$) and $d$ ($l = 2$) pseudopotentials $V_s(r)$, $V_p(r)$ contain no core cancellation in the sense of the cancellation theorem of pseudopotential theory [18], and one may therefore expect them to be similar. With $Q_c$ tuning it has been found that they can be made extremely similar, as shown in Fig. 4 for carbon using the parameters given in Table 2. The $V_{\mathrm{L}}(r)$ is then taken as $V_p(r)$ because the $l = 2$ components in the wave functions are presumed to be very small. This gave a logarithmic derivative for $l = 2$ practically identical to that from the $V_d$ pseudopotential and very close to the all-electron one by the standards of pseudopotentials. Similarly, very good pseudopotentials with only an $l = 0$ projector were also generated for C, N and O with the parameters of Table 2. Extensive tests were carried out on the C and O pseudopotentials for the work of Ref.[8] and on the N pseudopotential with methylamine [19].

Similarly with $Q_c$ tuning a pseudopotential was generated for Al with only the $l = 0$ part non-local, as given in Table 2. It has been well tested in solid state calculations and gives a satisfactory value for the $C_{44}$ elastic constant (correct to 10%) which is notoriously sensitive to the pseudopotential (Ref [19] p.IV-18). For Br with the parameters in Table 2 the local potential

$$V_{\mathrm{L}}(r) = \alpha V_p(r) + (1 - \alpha) V_d(r) \tag{3.1}$$

with $\alpha = 0.7$ gave good logarithmic derivatives for $l = 1$ and 2, again leaving only a projector for $l = 0$. This also avoided some problems in generating the Kleinman-Bylander form of the pseudopotential [9] for calculations, which was in fact the reason for generating it.

Table 1: The solid state bulk test of Cu pseudopotentials, comparing the results of the present calculations (first three rows) with those from another pseudopotential [11] and from an all-electron calculation (LAPW), and with experiment : for lattice constant $a$, bulk modulus $B$ and $B'$ the pressure derivative of bulk modulus fitted from the equation of state.

| Type | $E_{\text{cut}}(eV)$ | $a$(Å) | $B$(GPa) | $B'$ |
|---|---|---|---|---|
| $r_c(d) = 2.0$ a.u. | 1000 | 3.60 | 166 | 5.0 |
| $r_c(d) = 2.0$ a.u. | 650 | 3.59 | 163 | 5.4 |
| $r_c(d) = 2.4$ a.u. | 500 | 3.66 | 145 | 4.8 |
| | | | | |
| $r_c(d) = 2.3$ a.u.[a] | 982 | 3.60 | 160 | 5.1 |
| LAPW [b] | | 3.61 | 162 | |
| Experiment [c] | | 3.61 | 142 | 5.28 |

[a] Ref [11]

[b] Ref [16]

[c] Ref [17]

In the transition elements the $V_d$ pseudopotential is very different from the $V_s$ and $V_p$ ones, and it was found for Fe, Co and Cu the latter two could be well represented by the local potential

$$V_{\text{L}}(r) = \beta V_s(r) + (1 - \beta)V_p(r) \tag{3.2}$$

which leaves only a set of projectors for $V_d(r)$. The parameters are given in Table 2, the pseudopotential for Co having been tested by solid state calculations for the work on CoSi2 in Ref [20]. In Cu the $q_3$ for $l = 0$ was set equal to $q_2$ so that (1.1) effectively only contains two terms instead of three.

In Al and Ge, it was possible with $Q_c$ tuning to make the pseudopotentials for $l = 0$, 1 and 2 all quite similar, which would give a local potential if taken as equal. Such a potential is probably

Table 2: Parameters for pseudopotentials with projector reduction. The second column gives the label of the pseudopotential in Ref [19] where more details and tests may also be found. The third column gives the atomic wavefunction used for generating the $s$ and $p$ pseudopotentials, and the second line in the same column for $V_d(r)$. The values of $Q_c$ for $l = 0, 1, 2$ are given in the form of $Q_c/q_3(s, p, d)$. The last two columns give $\alpha$, $\beta$ in Eqs. (3.1), (3.2).

| Element | (Label) | Configuration $V_s$, $V_p$ | $V_d$ (if different) | $r_c(s, p, d)$ | $Q_c/q_3(s, p, d)$ | $\alpha$ | $\beta$ |
|---|---|---|---|---|---|---|---|
| B | B001a | $2s^{2.00}2p^{1.00}$ | $2s^{1.00}3d^{0.20}$ | all 1.4 | 0.80, 0.80, 1.00 | 1.0 | - |
| C | C021 | $2s^{2.00}2p^{2.00}$ | $2s^{0.75}2p^{1.00}3d^{0.25}$ | all 1.4 | 0.80, 1.05, 1.0325 | 1.0 | - |
| N | N010 | $2s^{2.00}2p^{1.00}$ | $2s^{0.75}2p^{2.00}3d^{0.25}$ | all 1.4 | 0.80, 1.05, 1.035 | 1.0 | - |
| O | O051 | $2s^{2.00}2p^{4.00}$ | $2s^{1.00}2p^{1.75}3d^{0.25}$ | all 1.4 | 0.40, 1.11, 1.0325 | 1.0 | - |
| Al | Al013a | $3s^{2.00}3p^{1.00}$ | no $d$ is used | all 2.4 | 1.10, 1.10 | - | 0.8 |
| Br | Br000 | $4s^{2.00}4p^{5.00}$ | $4s^{1.00}4p^{3.75}4d^{0.25}$ | all 1.4 | 1.00, 1.00, 0.90 | 0.7 | - |
| Fe | Fe002 | $3d^{4.00}4s^{1.00}4p^{0.25}$ | | all 2.4 | 0.48, 0.87, 1.18 | - | 0.3 |
| Co | Co013_v2 | $3d^{7.00}4s^{1.00}4p^{0.25}$ | | 2.0, 2.0, 2.4 | 0.70, 0.965, 1.18 | - | 0.2 |
| Cu | Cu006g | $3d^{9.00}4s^{0.75}4p^{0.25}$ | | 2.0, 2.0, 2.5 | 0.80, 0.95, 1.20 | - | 0.5 |

FIG.4

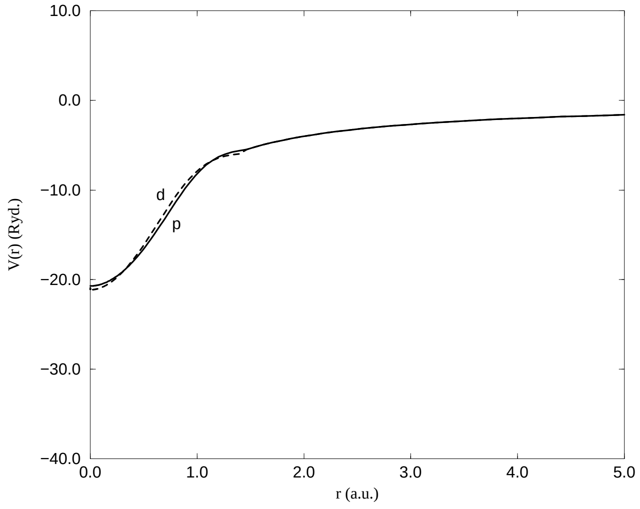

Figure 4: $V_{l=1}(r)$ (solid line) and $V_{l=2}(r)$ (dashed line) for carbon with the parameters of Table 2.

not good enough for modern work, but explains perhaps why empirical local potentials were found to give rather good results through the 1960's and 1970's and even more recently for Al, Ge and As [21, 22].

## 4 Discussion and Conclusion

In Section 2 we described how $Q_c$ may be varied to obtain the best fit to the logarithmic derivative of the original potential, and we turn now to look at how the variation of $Q_c$ manifests itself in the resultant pseudopotential as is required for projector reduction. Fig. 1 shows that the main effect of varying the Kinetic Energy Filter parameter $Q_c$ is to change the depth of the pseudopotential in $r$-space. One can interpret qualitatively the effect of the optimisation on the shape of a pseudopotential from an $r$-space view point, which is useful when using $Q_c$ to regulate the shape of the pseudopotential. If $Q_c$ is set to be relatively small, this pushes $\Psi_l(r)$ in the direction of having lower Fourier components, which means having lower kinetic energy inside $r_c$. Since the energy eigenvalue is fixed and is equal to the kinetic energy plus potential energy, the low kinetic energy implies a rather shallow (weak) pseudopotential. On the other hand using a higher $Q_c$ results in a deeper pseudopotential as shown in Fig. 1(c). If $Q_c$ is reduced even further, the pseudopotential becomes even shallower (weaker) and a barrier will be raised near $r_c$ as a result of the norm-conserving constraint so that the pseudopotential preserves the correct amount of charge within the pseudo-core region. Such a barrier may look strange but experience shows it does not affect $E_{\text{cut}}$ or the accuracy of the pseudopotential in solid state tests provided the logarithmic derivative fits well.

The effect of $Q_c$-tuning on the shape of a pseudopotential also depends on other factors. In the

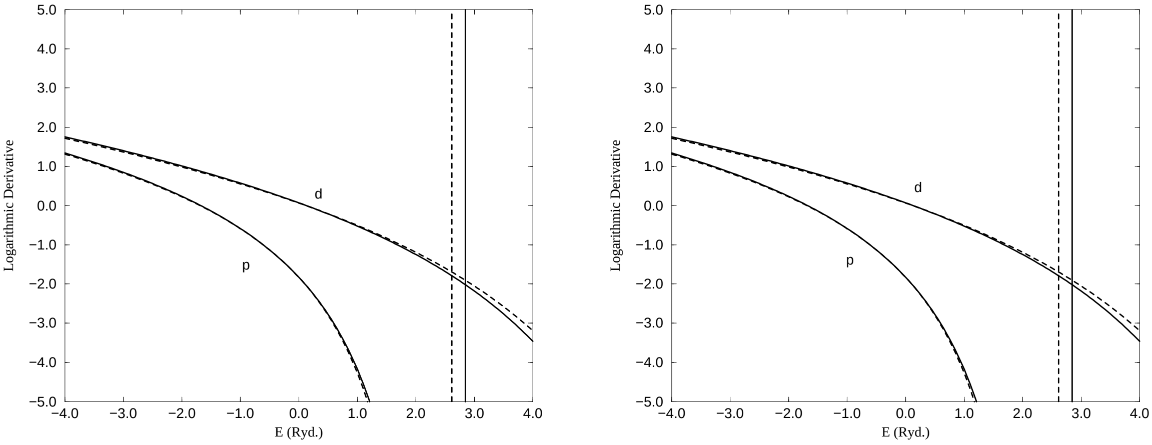
FIG 5(a)

FIG 5(b)

Figure 5: Logarithmic derivative of carbon before (a) and after (b) projector reduction.

case of nodeless orbitals such as $2p$ and $3d$, the pseudopotentials are highly attractive because there is no "Cancellation Effect" from inner shells in the sense of conventional pseudopotential theory [18]. Optimising these pseudopotentials therefore means shifting the electrons outward from the centres of the atoms. On the other hand, in the case of (soft) pseudopotentials that do have a cancellation effect from inner shells, using a smaller $Q_c$ means spreading the charge distribution inwards towards the centres of the atoms, which serves to lower the magnitude of the originally repulsive (or weakly attractive) pseudopotentials at $r = 0$, but has less effect on their shape near $r_c$. Such a trend can be used to systematically regulate the shape of a pseudopotential by tuning $Q_c$.

Figure 4 illustrates the use of $Q_c$ tuning to achive projector reduction. It shows $l = 1$ and $l = 2$ pseudopotentials $V_1(r)$ and $V_2(r)$ for C which have been tuned using $Q_c$ to resemble each other as close by as possible while retaining a good fit to the all-electron logarithmic derivative (Fig. 5). Tests showed that the resemblance was sufficiently good to use $V_1(r)$ also for $V_2(r)$ and for all higher $l$, i.e. to take it as the local component of the pseudopotential. Thus only one projector for $l = 0$ was required. The experience with generating pseudopotentials with reduced number of projectors for the elements listed in Table 2 suggests that this idea can probably be extended to a significant number of other elements.

The current scheme has been used to generate a significant number of pseudopotentials for a wide range of applications. A complete periodic table of pseudopotentials is available commerically from Molecular Simulation Inc. for use with the CASTEP code for solid state applications, though not all have been thoroughly tested. Nearly 300 papers have been published in the academic literature with calculations using pseudopotentials generated by the present method. We reference some of the early ones because they tend to contain more details of the pseudopotentials, namely those for Co [18]; Ge [21]; C, O and Pd [22]; Cu and Cl [23]. The pseudopotentials for C and O were tuned especially for projector reduction in the large dynamic calculation on a zeolite [8] as already mentioned. More details on 38 elements may be found in Ref [19].

The code for generating pseudopotentials by the present method will be available at the website http://www.phys.tku.edu.tw/qc/

In summary, therefore, we have introduced an improved scheme for generating Optimised Pseudopotentials. The $Q_c$ parameter is used in a new way, and is tuned to give as accurate a pseudopotential as possible, meaning a good match to the all-electron logarithmic derivative of the wave function over a suitably wide range of energy. The continuity constraint of $\Psi_l''(r)$ at $r_c$ is dropped and the number of terms in the expansion (1.1) is also reduced to three, to remain equal to the number of constraints in order to give a numerically stable algorithm. The reduction to three terms automatically tends to make the pseudopotential softer because the cut-off $E_{\rm cut}$ in solid state applications is largely controled by the highest qi appearing in (1.1). Dropping the constraint on continuity of the $\Psi_l''(r)$ means the pseudopotential has a discontinuity at $r_c$, but in practice the $Q_c$ is tuned in our scheme to match the logarithmic derivative which always makes the discontinuity small, so that it does not adversely affect the accuracy or the softness of the pseudopotential. In some sense the dropping of one constraint allows the pseudo wavefunction (and hence pseudopotential) greater freedom for optimisation with regard to accuracy and convergence properties.

A most important point is that the generated pseudopotential and the corresponding logarithmic derivative vary with the chosen $Q_c$ parameter in a systematic way. One therefore has a well controlled situation for generating and improving a pseudopotential for any given physical application, depending on the required balance between $E_{\rm cut}$, the accuracy of the pseudopotential and the width of the energy range over which it has to be accurate. This is important for many calculations. Moreover we have shown how one can physically understand the connection between $Q_c$ and the shape of the pseudopotential, which helps one to operate the scheme systematically and efficiently. The scheme represents a further significant step toward generating systematically good norm-conserving pseudopotentials for a wide variety of physical systems. We have also demonstrated how to use $Q_c$ tuning method to reduce the number of non-local projectors of pseudopotentials for quite a few elements. These projector reduced pseudopotentials allow one to save significant computing time while remain as accurate as normal unreduced ones.

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## References

[1] A. M. Rappe, K. M. Rabe, K. Kaxiras and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990).

[2] A. M. Pappe and J. D. Joannopoulos, in Computer Simulation in Material Science, edited by M. Mayer and V. Pontikis, pp. 409-422 (Kluwer, Dordrecht, 1991).

[3] J.-S. Lin, A. Qteish, M. C. Payne and V. Heine, Phys. Rev. B **47**, 4174 (1993).

[4] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[5] C. Pickard (private communication).

[6] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[7] M. C. Payne, M. P. Teter, D. C. Allen, T. A. Arias and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[8] R. Shah, M.C. Payne, M.-H. Lee and J.D. Gale, Science 271, 1996 (1996); R. Shah, J.D. Gale and M.C. Payne, J Phys. Chem. B **100**, 11688 (1996); Int. J. Quantum Chem. **61**, 393 (1997); J. Phys. Chem. B **101**, 4787 (1997); J.D. Gale, R. Shah, M.C. Payne, I. Stich and K. Terakura, Catalysis Today **50**, 525 (1999).

[9] L. Kleinman and D. M. Bylander, Phys Rev. Lett. **4**, 1425 (1978).

[10] R.D. King-Smith, M.C. Payne and J.-S. Lin, Phys. Rev. B **44**, 13063 (1991).

[11] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[12] P. E. Blöchl, Phys. Rev. B **41**, 5414 (1990).

[13] D. R. Hamann, M. Schluter and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[15] M. J. Gillan, J. Phys : Condensed Matter **1**, 689 (1989); A. De Vita, Ph.D. thesis, Keele University, 1992.

[16] Z. W. Lu, S. -H. Wei, and A. Zunger, Phys. Rev. B **41**, 2699 (1990).

[17] P. van 't Kiooster, N. J. Trappeniers, and S. N. Biswas, Physica B **97**, 65 (1979).

[18] V. Heine, Solid State Physics **24** , 1 (1970).

[19] M.-H. Lee, Ph.D. thesis, Cambridge University, 1995.

[20] V. Milman, M.-H. Lee, and M. C. Payne, Phys. Rev. B **49**, 16300 (1994).

[21] I. J. Robertson, M. C. Payne and V. Heine, Europhys. Lett. **15**, 301 (1991).

[22] M. Needels, M.C. Payne and J. Joannopoulos, Phys. Rev. B **38**, 5543 (1988).

[23] V. Milman, D. E. Jesson, S. J. Pennycook, M. C. Payne, M.-H. Lee, I. Stich, Phys. Rev. B **50**, 2663 (1994).

[24] P. Hu, D. A. King, S. Crampin, M. -H. Lee and M. C. Payne, Chem. Phys. Lett. **230**, 501 (1994).

[25] H.-C. Hsueh, J. R. Maclean, G. Y. Guo, M. -H. Lee, S. J. Clark, G. J. Ackland and J. Crain, Phys. Rev. B **51**, 12261 (1995).