# Atomic pseudo-Hamiltonians for Quantum Monte Carlo

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## Abstract

Quantum simulations, successful for simple systems, remain difficult for atoms with core electrons. We discuss the possibility of replacing core electrons by a local yet angular-momentum dependent pseudo-Hamiltonian where momentum operators appear only to the second power, as required by fixed-node Quantum Monte Carlo. We describe two ways of constructing it from norm-conservin g local-density atoms: a simpler approach, which works for $s$-$p$ atoms, and a more sophisticated one, based on a simulated-annealing technique, which fixes $s$, $p$ and $d$ states. The use of this new pseudo-Hamiltonian in Green's Function Monte Carlo (both fixed-node and release-node) gives accurate electron affinities, ionization and binding energies for second-row atoms and diatomics. This opens the way to quantum simulations of many condensed-matter systems.

## 1. Introduction

Quantum Monte Carlo (QMC) methods, in particular Green's Function Monte Carlo, can achieve remarkable accuracy for total ground s tate energies including correlation effects that are left out or approximated by other computational methods such as Hartree-Fock, or local-density-functional theory and can treat systems of up to 1000 electrons, far beyond the capabilities of configuration-interaction methods. Examples of such calculations include the ground state properties of liquid and solid $^3$He and $^4$He (Kalos *et al.* 1974), the homogeneous electron gas (Ceperley and Alder 1980), solid hydrogen at high pressures in the molecular and atomic phases (Ceperley and Alder 1987), and many small molecules (Anderson 1975, Reynolds *et al.* 1982, Moskowitz *et al.* 1982). However, the presence of atomic cores slows the convergence of the simulation to such an extent that calculations of atoms heavier than neon appear not to be feasible. There are several related problems (Ceperley 1986):

(i) the distances and energies of the $1s$ electrons determine the time step of the simulation and these scale with the atomic number as $Z^2$

(ii) the statistical errors are proportional to the correlation energy, which, for $Z < 20$, increases as $Z^{1.5}$, while the physically relevant valence energies are more or less constant throughout the periodic table; finally

(iii) the computational effort per step of the simulation increases as the total number of electrons cube.

Combining all the effects the total computational effort shows a very strong dependence on the atomic number Z; estimates are between $Z^{5.5}$ (Ceperley 1986) and $Z^{6.5}$ (Hammond *et al.* 1987). It is then very desirable to eliminate the core electrons completely which will hopefully allow Monte Carlo (MC) simulations of heavier atoms in extended systems.

Pseudopotentials, model potentials or frozen core approximations have a very long history (see e.g. Cohen and Heine 1970, Heine and Weaire 1970, Bassani and Pastori Parravicini 1974, Schlüter and Sham 1982); the state of the art is such that much more serious approximations are made today in solving the correlated atom than in reducing an atom to a pseudoatom. Modern pseudopotentials, born within local-density-functional or Hartree-Fock theory, (see e.g. Bachelet *et al.* 1982, and references therein) have been successfully tested in the context of variational MC calculations by Fahy *et al.* (1988); however, being nonlocal (they contain angular-momentum projection operators), they are generally inappropriate for QMC simulations. To extend the concepts of modern pseudopotential theory to QMC simulations (and in general beyond single-particle theory) the development of entirely new theoretical and computational tools is required (Bachelet *et al.* 1988, Hammond *et al.* 1988). What we present in this paper is the possibility of totally replacing the core electrons by a local yet angular-momentum dependent atomic Hamiltonian in such a way that the methods developed for QMC are still applicable.

## 2. Green's Function Monte Carlo

In Green's Function Monte Carlo (Ceperley and Kalos 1979) one begins by sampling an ensemble of configurations $R$ ($R$ is the set of $3N$ coordinates and $N$ is the number of electrons) from some arbitrary probability distribution $f_{\rm o}(R)$. This probability distribution is then iterated:

$$f_{n+1}(R) = \int G(R, R'; t) f_n(R')\, dR' \quad , \tag{1}$$

where $n$ is the iteration number and $G$ the Green's function:

$$G(R,R';t) = \Psi(R)\Psi(R')^{-1} < R \mid \exp[-t(H-E_T)] \mid R' > \quad . \tag{2}$$

Here $\Psi(R)$ is the trial function, $H$ the Hamiltonian, $t$ the time-step (the imaginary or thermal time-step) and $E_T$ the trial energy. At large $n$, $f_n(R)$ approaches $\Psi(R)\Phi_o(R)$ where $\Phi_o(R)$ is the ground state wave function. As the trial function approaches the ground state wave function the variance of the estimate of the ground state vanishes. This is the chief motivation for applying importance sampling and makes QMC simulations of large systems practical.

The main limitation of Green's Function Monte Carlo arises from the need to keep the Green's function non-negative (Schmidt and Kalos 1984) so that it can be sampled as a probability distribution. One can, in fact, treat Green's functions with negative pieces; one simply samples the ab solute value of $G$ and carries along the sign as a weight. However, for large values of $n$ this gives rise to an exponentially growing noise. In condensed matter physics, this procedure is known as either the release-node (Ceperley and Alder 1984) or the transient-estimate (Schmidt and Kalos 1984) method. Such methods are not appropriate for large systems, since the statistical error grows rapidly with the number of particles.

Any fermion system will have a Green's function with negative pieces because the trial function changes sign whenever two electrons with the same spin exchange. The fixed-node approximation (Anderson 1975, Ceperley and Alder 1980, Reynolds *et al.* 1982, Moskowitz *et al.* 1982) is made in order to treat these systems. There one divides the configuration space into two volumes: a region where $\Psi(R)$ is positive, and a region where $\Psi(R)$ is negative. The fixed-node Hamiltonian equals $H$ for matrix elements within the same region but matrix elements from one region to the other are set to zero. There are three important properties of this approximation:

(1) The fixed-node Green's functions is non-negative so that the error wi ll decrease inversely proportional to the square root of the number of steps of the random walk.

(2) The fixed-node energy is an upper bound (Ceperley and Kalos 1979) to the true fermion energy: $E_{FN} \geq E_{\rm o}$.

(3) As the nodes of $\Psi$ approach the nodes of $\Phi_{\rm o}$ (i.e. the region where $\Phi_{\rm o}\Psi$ is negative vanishes) $E_{FN} - E_{\rm o}$ vanishes quadratically. Only the position of the nodes is important, not the values of the trial function anywhere else.

The first property allows one to simulate many-fermion systems: the second and third show the method is variational. In fact, in most systems the error introduced by the fixed-node approximation is extremely small. The use of Hartree-Fock *nodes* will give 99% of the correlation energy for typical el ectronic systems (Reynolds *et al.* 1982, Moskowitz *et al.* 1982).

### 3. Atomic pseudo-Hamiltonians and quantum Monte Carlo

We show here that to preserve the three properties discussed at the end of the previous section the Hamiltonian must be local and contain at most second derivatives. If $H$ is a non-local Hamiltonian, and its matrix elements between the two regions are deleted, properties (2) and (3) will not hold in general. For that reason we restrict ourselves to local Hamiltonians only. Such a Hamiltonian can be expanded in powers of momentum operators:

$$H = g(R) + \sum_a g_a(R) p_a + \sum_{a,b} g_{ab}(R) p_a p_b + \ldots \quad . \tag{3}$$

Now for (1) to hold $G(R, R_{\rm o}; t)$ must be positive for all $R$ and $R_{\rm o}$ in the same region. Suppose we construct the second moment of $G$ about $R_{\rm o}$,

$$c_{ab}(R_{\rm o};t) = \int (R-R_{\rm o})_a (R-R_{\rm o})_b G(R,R_{\rm o};t)\, dR \quad . \tag{4}$$

This tensor must be positive definite for all trial functions (except if $\Psi(R_{\rm o})=0$), and times $t$; since it vanishes at zero time ($G$ reduces to a delta function), the derivative of $c$ at zero time must be positive definite. This can be explicitly evaluated to give:

$$\left.\frac{dc_{ab}}{dt}\right|_{\rm o} = \Psi^{-1}\left(\frac{\partial^2 H}{\partial p_a \partial p_b}\right)\Psi \quad , \tag{5}$$

where first we take the time derivative of Eq. (4), use the definition of $G$, Eq. (2), the hermitian property of $H$, and then commute the $R$'s with the momentum operators. Suppose the highest power of the momentum in $H$ is $n$. Then $dc/dt|_{\rm o}$ will be proportional to the $(n-2)$th derivative of the trial function and, unless $n=2$, $dc/dt|_{\rm o}$ (and thus $c$) cannot be made positive definite for *all* choices of the trial function which, in turn, implies that $G$ will have negative pieces. In conclusion, for $G$ to be positive for all $R$ and $R_{\rm o}$ in the same region, it is necessary that $n=2$ and that the tensor $\left(\partial^2 H/\partial p_a \partial p_b\right)$ be positive definite. The above three requirements and hermiticity lead to the following general form of a Hamiltonian:

$$H = V(R) + \sum_{a,b} p_a g_{ab}(R) p_b \tag{6}$$

where the tensor $g_{ab}$ is positive definite. To simplify further, suppose that the pseudo-Hamiltonian (PH) for a collection of atoms has the same structure as the full Hamiltonian:

$$H = \sum_{i<j}\frac{1}{r_{ij}} - \frac{1}{2}\sum_i \nabla_i^2 + \sum_{i,I} h_I(r_{iI}) \quad . \tag{7}$$

Atomic units are used throughout this paper, $i$ and $j$ refer to electrons and $I$ to ions. The most general form of the atomic PH with these properties (and spherical symmetry) is:

$$h(r) = -\frac{1}{2}\nabla a(r)\nabla + \frac{b(r)L^2}{2r^2} + v(r) \quad , \tag{8}$$

where $a(r)$, $b(r)$ and $v(r)$ are radial functions, and $L^2$ is the usual angular momentum operator. Since the tensor $\left(\partial^2 H/\partial p_a \partial p_b\right)$ must be positive definite we require:

$$a(r)+1>0\,, \quad a(r)+b(r)+1>0 \quad . \tag{9}$$

Notice that if the above requirement is not fulfilled the Hamiltonian is not bounded below. On physical grounds it is rather evident that outside the core of an atom $a$ and $b$ will vanish and $v=-Z_v/r$ ($Z_v$ is the valence charge). By modifying the kinetic energy operator inside the atomic cores we are, in effect, making the electronic mass position and direction dependent. This is to be distinguished from a momentum dependent mass (see e.g. Cohen and Heine 1970) which would not lead to a suitable Hamiltonian.

We have argued that there is very little freedom in choosing the PH once one has accepted conditions 1-3 and that it be a sum of atomic Hamiltonians. One possibility is to keep 1-3 but make the local potential a more general function of $R$; for example, one could modify the electron-electron interaction inside the core to mimic the effects of core polarizability. We do not consider such a possibility here. Other authors (Hurley and Christiansen 1987; Hammond *et al.* 1987) have made a local potential by projecting a non-local potential onto a Hartree-Fock trial function. That doe s not satisfy conditions (2) or (3) since it requires the trial function be accurate everywhere, not just at the node.

## 4. Atomic pseudo-Hamiltonians and norm-conserving pseudopotentials

Our general goal is to replace the true system (a full-core atom) with a pseudo system (a valence-only atom). The latter should ideally reproduce the behavior of the former outside the core region in a wide variety of situations: not only for a *reference atomic configuration* (e.g. the ground-state valence configuration), but also in a molecular or solid-state environment. In other words the ideal atomic PH, though energy independent,

is highly transferable: it should closely track the true Hamiltonian over a wide range of energies around the atomic ground state, so that, even if the formation of bonds and bands shifts the energy eigenvalues away from the atomic ground state, the pseudoatom continues to behave like the true, full-core atom.

Hamann, Schlüter and Chiang (1979) have shown that, whenever the many-body problem is reduced to a set of self-consistent single-particle equations (for example in local-density-functional or Hartree-Fock theory), the above requirement is met by norm-conserving pseudopotentials, which, for a given valence configuration, identically reproduce the valence states of a full-core atom outside the core: this ability also ensures optimum transferability, because of a remarkable relation between the integral of the wavefunction squared and the energy derivative of the logarithmic derivative of the wavefunction (see e.g. Landau and Lifschitz 1966). Norm-conserving pseudopotentials are such that, for each angular momentum $\ell$ which is relevant to the valence properties of the atom, the bound-state eigenvalue $\varepsilon_\ell$ is identical for either pseudo ($PS$) or full-core atom ($FC$), and, which is very important, outside some core radius $r > r_c$ the normalized radial wavefunction $r\chi_\ell$, and thus the logarithmic derivative $\chi_\ell'/\chi_\ell$, are identical:

$$\chi_\ell^{PS}(r) \equiv \chi_\ell^{FC}(r) \quad ; \quad \left[\frac{\chi_\ell{}'(r)}{\chi_\ell(r)}\right]^{PS}_{\varepsilon\,=\,\varepsilon_\ell} \equiv \left[\frac{\chi_\ell{}'(r)}{\chi_\ell(r)}\right]^{FC}_{\varepsilon\,=\,\varepsilon_\ell} \quad , \tag{10}$$

Away from $\varepsilon_\ell$ discrepancies are only second order in th e energy $\varepsilon - \varepsilon_\ell$, because Eq. (10) plus normalization implies that the first energy derivative is identical at $\varepsilon_\ell$ (Hamann *et al.* 1979):

$$\frac{d}{d\varepsilon}\left[\frac{\chi_\ell{}'(r)}{\chi_\ell(r)}\right]^{PS}_{\varepsilon\,=\,\varepsilon_\ell} \equiv \frac{2}{\chi_\ell^{PS}(r)}\int_0^{r_c} dr'[\chi_\ell^{PS}(r')]^2 \equiv \frac{2}{\chi_\ell^{FC}(r)}\int_0^{r_c} dr'[\chi_\ell^{FC}(r')]^2 \equiv \frac{d}{d\varepsilon}\left[\frac{\chi_\ell{}'(r)}{\chi_\ell(r)}\right]^{FC}_{\varepsilon\,=\,\varepsilon_\ell} \quad . \tag{11}$$

As mentioned, the exact fulfillment of the above conditions is relevan t only for angular momenta which correspond either to occupied valence orbitals in the atom, or to empty

orbitals whose energy is low enough to be potentially involved in the bonding process. This gives angular-momentum dependent nonlocal pseudopotentials, reflecting the physical fact that different partial waves feel the effect of orthogonality to different core shells. For most atoms excellent norm-conserving pseudopotentials are obtained by imposing Eqs. (10,11) to $s$, $p$ and $d$ pseudowavefunctions (see e.g. Bachelet *et al.* 1982); for many atoms it may be sufficient to fix only $s$ and $p$ waves.

Since local-density-functional and Hartree-Fock theories successfully describe many properties of atoms, molecules and solids, it is very likely that the angular-momentum dependence is a general property of transferable PH's and is needed in the exact many-body theory. The fact that the bare-ion pseudopotentials derived from either local-density-functional or Hartree-Fock theory are essentially identical (Gygi and Baldereschi 1986) in spite of the different approximations involved in the two approaches further suggests that the norm-conserving pseudopotentials derived in that context represent an excellent approximation to their general many-body counterpart.

In a single-particle theory like local-density-functional theory the form of our PH allows us in principle to fix up to three partial waves. The radial Schrödinger equation for a single-particle state of angular momentum $\ell$ is for our PH:

$$\left[-\frac{1}{2}(a+1)\frac{d^2}{dr^2}+(a+b+1)\frac{\ell(\ell+1)}{2r^2}-\frac{1}{2}\frac{da}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)+v+v_{HXC}\right]\chi_\ell=\varepsilon_\ell\,\chi_\ell \quad , \quad (12)$$

where $v_{HXC}$ is the sum of the Hartree and exchange-correl ation potentials. We determine the three functions $a$, $b$ and $v$ by demanding that, in a given valence configuration, the self-consistent valence eigenvalues and radial eigenfunctions which solve Eq. (12) be identical to those of some norm-conserving $\ell$-dependent pseudopotential $v_\ell(r)$ (see e.g. Bachelet *et al.* 1982) . Subtract the pseudopotential Schrödinger equation from Eq. (12): $v_{HXC}$ and $\varepsilon_\ell$

drop out and

$$\left[-a\frac{d^2}{dr^2}+(a+b)\frac{\ell(\ell+1)}{r^2}-\frac{da}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)+2(v-v_\ell)\right]\chi_\ell=0 \quad . \tag{13}$$

If the *reference atomic configuration* contains $s$, $p$ and $d$ orbitals, Eq. (13) gives for $\ell=0,1,2$ three conditions for the three functions $a$, $b$ and $v$, which are thus uniquely determined: one gets a first order differential equation for $a$ and, once that is solved, $b$ and $v$ are obtained in terms of $a$, $da/dr$ and combinations of pseudopotentials and self-consistent wavefunctions. From their form one recognizes that $a$, $b$ and $v$ automatically recover correct behavior outside the core ($a\to 0$, $b\to 0$, and $v\to -Z_v/r$ for $r>r_c$).

It appears that we have a prescription to build up a local norm-conserving Hamiltonian which exactly mimics the action of an $\ell$-dependent, nonlocal pseudopotential for the three partial waves $s$, $p$ and $d$, and thus excellent for the vast majority of atoms (only lanthanides, rare earths and few other atoms really need an accurate $f-$wave, and, for these atoms, pseudopotentials are less accurate anyway: see e.g. Bachelet *et al.* 1982). Unfortunately upon actual calculations it turns out that the $a$ and $b$ functions resulting from Eq. (13) for $\ell=0,1,2$, do not satisfy the conditions of Eq. (9) for many atoms and various types of norm-conserving pseudopotentials. Fortunately, as already mentioned, there is a large class of atoms which form $s$-$p$ bonded molecular and solid-state systems, and for them two partial waves are usually sufficient. As a first attempt we can then concentrate on these atoms, and, instead of fixing three partial waves ($s$, $p$ and $d$) we only focus on two of them ($s$ and $p$). We drop the differential equation for $a$, and with some trial and error choose the simple analytic form $a=a_{\rm o}\exp[-(r/r_c)^k]$ which vanishes outside the core ($r>r_c$). Now Eq. (13) can be used to fix exactly two partial waves (e.g. $s$ and $p$). The three parameters $a_{\rm o}$, $r_c$ and $k$ are chosen such that

(i) the range of $a(r)$ roughly agrees with the physical extent of the atomic core

(ii) Eq. (9) is satisfied, and

(iii) the $d$ states are reasonably reproduced.

Our choice of $a_o$, $r_c$ and $k$ is shown in Table I for Na, Mg, Si and Cl; the radial functions $a$, $b$ and $v$ are shown in Fig. 1 for Si. The Si logarithmic derivatives, important for transferability, are plotted against energy in Fig. 2, and show that the new PH is of comparable quality as the original, nonlocal pseudopotential.

## 5. Second-row $s$-$p$ atoms and molecules

Now we present some tests of our new pseudo-Hamiltonian: a set of QMC calculations for second-row atoms and diatomic molecules (Bachelet *et al.* 1988). Our MC calculations have been performed with a simple generalization of the diffusion MC algorithm (J.B. Anderson 197; Ceperley and Alder 1980; P.J. Reynolds *et al.* 1982; Moskowitz 1982). This makes an approximation to the Green's function of Eq. (1) which is exact in the limit of small time steps. The more rigorous and efficient, but complicated, Domain Green's Function Monte Carlo algorithm would dispense with this time-step error (Kalos *et al.* 1974). In either algorithm there are three basic steps: branching, diffusion and drift. The program for the PH runs somewhat slower than one with a constant mass for these small systems but for a large system there will be no appreciable increase in computational time. We have used the same trial wave function employed in other QMC calculations (P.J. Reynolds *et al.*); a pair-product, Slater-Jastrow function, where the molecular orbitals are linear combinations of the single particle local-density-functional orbitals. The parameters in this trial function are fixed by minimizing the variational energy with the reweighting method (Ceperley and Kalos 1979). For atoms we use a minimum basis set while for molecules we add a few extra $p$ functions in the bond direction and a Gaussian in the middle of the bond. This type of functions works well if $a(r)$ does not approach $-1$, but

for Cl the pair correlation term should include some radial dependence to account for the sizable change of the effective mass in the core.

Variational MC (evaluation of the trial function energy), fixed-node diffusion MC and release-node MC calculations have been performed on the atoms and molecules shown in Table II. Release-node calculations were performed to determine the accuracy of the PH and of the fixed-node approximation. It is possible to converge to the exact energy, but that procedure becomes more costly for systems with more electrons. The calculations shown took between 1 minute of CRAY time (for Na) to 2 hours (for $Cl_2$).

The accuracy of the PH varies. The electron affinities are in perfect agreement with experiment (Weast 1988) to the accuracy shown (which varies from 0.7 mH for Na to 4 mH for Cl). The same holds for the first ionization potentials of Si and Cl, while the experimental ionization potential of Na and Mg is outside the QMC error bar by 6 mH and 4 mH respectively. The homo-nuclear diatomic binding energies are in excellent agreement with experiment for $Si_2$, $Cl_2$ and $Mg_2$, but 10% too low for $Na_2$. This discrepancy may be related to the problems pointed out by Louie *et al.* (1982) for atoms with few valence electrons. Fig. 3 compares the $Si_2$ binding energy curve as calculated with PH-QMC and the configuration-interaction method (McClean *et al.* 1984).

## 6. Further refinements: $s, p$ and $d$ exact

As already mentioned, if one looks for the exact solution of Eq. (13) using available $s$, $p$ and $d$ norm-conserving atomic wavefunctions (as obtained e.g. following Hamann *et al.* 1979 or Kerker 1980), then the resulting radial functions $a(r)$, $b(r)$ and $v(r)$ do not fulfill the conditions of Eq. (9). However the pseudopotential constructions suggested by Hamann *et al.* in 1979, or by Kerker in 1980, are only two convenient procedures; many other valid schemes can in principle be conceived. Norm-conserving pseudopotentials are

by no means uniquely defined inside the core, and, on the contrary, for each atom there exists a large class of equivalent norm-conserving pseudopotentials whose eigenfunctions fulfill Eqs. (10,11) but differ from each other inside the core. So instead of keeping the existing pseudopotentials and giving up the $d$ orbitals, as successfully done in the previous two sections for $s$-$p$ atoms, one may well consider a more general construction: starting from a full-core local-density-functional atom one has to find a set of $s$, $p$ and $d$ pseudowavefunctions which not only enjoy the property of "conserving the norm" Eqs. (10,11), but also, when plugged into Eq. (13), will yield radial functions $a(r)$, $b(r)$ and $v(r)$ which fulfill the conditions of Eq. (9). That such a set of pseudowavefunctions exists at all is neither obvious nor easy to derive from our formulae: after expressing the conditions of Eq. (9) in terms of pseudowavefunctions one finds a rather discouraging nonlinear inverse-scattering problem. But the question is a very interesting one because it crucially affects the possibility of using the local pseudo-Hamiltonian of Eqs.(8,9) for $d-$metals. Two of us (Mitáš and Bachelet 1989) have recently proposed to attack this problem from the numerical side, by a simulated-annealing technique (Kirkpatrick *et al.* 1983, Černý 1982, 1985 and Černý and Novák 1986). The $s$, $p$ and $d$ radial wavefunctions are expressed in the Kerker form

$$\chi_\ell^{PS}(r) = r^{\ell+1} \exp\left[p_\ell(r)\right] \tag{14}$$

inside the core ($r < r_c$), but, instead of using polynomials or othe r analytic functions which would considerably limit the variational flexibility, the three optimal $p_\ell$ functions ($\ell = 0, 1, 2$) are searched among all the continuos bounded functions (with continuous first derivative) which fulfill the matching condition in $r_c$ and the condition $p_\ell{}' = r^\alpha$ with $\alpha \geq 1$ in the origin (which ensures that the pseudopotentials $v_\ell$ and the radial functions $a$, $b$ and $v$

remain finite in the origin). On the computer these radial functions may be represented on a sufficiently dense regular grid. Both the norm conservation Eq. (11) and the conditions on $a$ and $b$ expressed by Eq. (9) are then imposed via simulated-annealing techniques: first a suitable energy (or cost) function is defined, which by construction is zero when all conditions are satisfied and is otherwise always positive ($C$ is a positive constant):

$$E_{cost} = E\left[a+1\right] + E\left[a+b+1\right] + \sum_{\ell=0,1,2} N_\ell \tag{15}$$

$$E\left[f\right] = C \int_0^{r_c} f(r)\left(sign[f(r)] - 1\right) dr \tag{16}$$

$$N_\ell = \left| \int_0^{r_c} \left( \left[\chi_\ell^{PS}(r)\right]^2 - \left[\chi_\ell^{FC}(r)\right]^2 \right) dr \right| \tag{17}$$

Then an appropriate dynamics in the space of the $p_\ell$ functions allows them to slowly relax towards the minimum-energy configuration. What is the meaning of the minimum-energy configuration? In principle there are two possibilities. If the minimum energy is $E_{cost} > 0$, then the norm conservation Eq. (11) and the conditions expressed in Eq. (9) are incompatible with each other, and the sought solution does not exist; the corresponding set of three $p_\ell$'s will only represent some trade off between Eq. (11) and Eq. (9). If, instead, the minimum energy is $E_{cost} = 0$, then the corresponding $p_\ell$'s are such that the conditions of Eqs.(9) and (11) are fulfilled, and an exact solution to our problem has been found. In practice, on the computer, we will stop the simulation run as soon as $E_{cost}$ reaches zero within some desired accuracy.

In passing we would like to point out that the power and generality of the proposed simulated-annealing method in the context of pseudopotential approach is by no means exhausted by the present application. It is possible to find more appropriate

representations of the involved functions and/or better strategy for movements on the configuration space; only the most necessary terms were incorporated in the definition of the energy Eqs. (15-17), but other terms can be included too - for example, terms which can increase the smoothness of the pseudo-Hamiltonian functions or which can limit a range of the function values. More generally, a very large variational freedom of the method can be used to further optimize traditional pseudopotentials; for example, to maximize their smoothness.

## 7. Open problems for $d$-metals

After solving the $d$-wave problem (applications to silicon will be presented in the next section) let us mention a severe problem which remains to be faced when studying transition elements, especially those of the first row (Sc through Cu); this problem, quickly mentioned at the end of Sec. 5, may also affect $s$-$p$ atoms with few valence electrons and a shallow underlying core (like Na). For these systems an accurate set of norm-conserving $s, p$, and $d-$waves for a given valence configuration (the so-called *reference atomic configuration*, for which the pseudopotential and the pseudo-Hamiltonian are constructed) may not be sufficient to ensure optimum transferability, as pointed out by Louie

*et al.* (1982): whenever significant core-valence overlaps occur, the linearization of the core-valence exchange potential, implicit in the "unscreening" procedure, becomes a questionable approximation (see also Greenside and Schlüter 1983). Within local-density-functional theory a cure to this problem was proposed by Louie *et al.* (1982) and successfully applied by Greenside and Schlüter (1983) to first-row transition elements. This cure can be extended to variational MC (Louie 1989) but again not to general QMC techiques, and something else has to be invented. One possibility is to give up pseudoatoms and try some frozen-core approximation, as proposed by Hammond *et al.* (1988); the

comparison of their results with ours (the benchmark being the Si atom) suggests however that a much larger error bar will result. Another possibility , which two of us are presently testing for Cu, (Mitáš and Bachelet 1989), is to include the shallow cores in the valence shells, as e.g. done by Starkloff and Joannopoulos (1977). This, as expected, works quite well, but the price is the inclusion of eight more electrons per atom (the underlying *s-p* core), which also will increase the error bar in QMC simulations. In few words, this is an open problem which requires new ideas.

## 8. Results for the silicon atom and conclusions

We illustrate the results obtained by the method presented in Sec. 6 for the case of silicon. For the atom we have used the ionized configuration $Si^{2+}$ ($3s^1\ 3p^{0.75}\ 3d^{0.25}$) with common $r_c = 1.75$ *a.u.* After some experience we have realized that the conditions of Eq. (9) are much more difficult to fulfill than the norm conservation Eq. (11). Since then we have started the simulations from configurations which fulfill Eq. (9) but not the norm conservation, and used a value of $C = 1000$ in Eq. (16). In this way during the simulation run $a(r)+1$ and $a(r)+b(r)+1$ remained positive as required by Eq. (9), due to the strong effect of the term Eq. (16) in the energy-cost function, while the norms slowly converged towards their correct values. For the silicon atom we stopped the simulation when the value of $E_{cost}$ was in the range of $10^{-4}$, entirely due to small residual discrepancies in the norms. The functions obtained are shown in Fig. 4. The functions exhibit larger variations than usual pseudopotentials. However, the corresponding pseudo wavefunctions (Fig. 5) are smooth and similar to those produced by "traditional" norm-conserving pseudopotentials (Hamann *et al.* 1979, Kerker 1980). With this new set of $a$, $b$ and $v$ functions we have performed some preliminary diffusion MC simulations for $Si^{2+}$. This is especially simple because with two valence electrons the spatial part of the wavefunction never changes

sign and one does not need any importance sampling; the diffusion MC is as simple as in the $H_3^+$ calculations of Anderson (1975), except that a spatially varying mass has to be introduced. The result obtained for the third ionization potential $1.222 \pm 0.021$ a.u. is in excellent agreement with the experimental value of 1.230 a.u. (Weast 1988). Compared to straight diffusion MC there are higher demands on the computer time essentially because of the rapidly varying mass inside the core.

The Si results just presented are evidently preliminary, but rather encouraging: the new local pseudo-Hamiltonian Eq. (8) can reproduce the action of a nonlocal norm-conserving pseudopotentials for all three partial waves in the test case of silicon and gives excellent results for the two-electron $Si^{2+}$ pseudoatom. Tests of this new pseudo-Hamiltonian for less simple physical systems and for various atoms, are underway.

A separate test which has its own interest concerns the one-electron excitations of the $Si^{3+}$ pseudoatom. In Table III we compare the results of norm-conserving pseudopotentials, the pseudo-Hamiltonian Eq. (8) obtained in Sec. 4 (Fig. 1), and the pseudo-Hamiltonian obtained here (Fig. 5). What we do is to solve the Schrödinger equation for one electron in the field of the bare pseudoion $Si^{4+}$ in the ground state and various excited states, for which detailed experimental results are available (Bashkin and Stoner 1975).

Comparing the various pseudoions considered in Table III it appears that the $s, p, d$ pseudo-Hamiltonian (PH-2) works much better than the $s$-$p$ one (PH-1) for $d$–states, as expected. But besides that a more general message comes from Table III: the remarkable agreement with the experiment up to very high excitation energies suggests that bare pseudoions obtained from a local-density-functional atom behave almost as real physical objects; in other words, it confirms that the core-valence interaction may be well represented (and then unscreened) within single-particle approximations. This was also indirectly confirmed by the good results of our QMC-PH calculations for many-electron

atoms and molecules (Table II, Fig. 3 and this section), which, on the other hand, also showed that an exact description of valence-valence interaction is of crucial importance for a more accurate description of condensed matter systems. By an exact treatment of valence electrons, in fact, pathological features of local-density-functional and Hartree-Fock theory (see e.g. Perdew and Zunger 1981) have disappeared: for example, our negative ions are bound and the calculated electron affinities are in good agreement with experiment; binding energies of our molecules are generally good and do not suffer from the overbinding which results from local-density-functional calculations (Martins *et al.* 1985, Jones 1985, 1987).

In conclusion we have presented a method which successfully eliminates core electrons from *s*-*p* atomic systems. Some challenges related to transition elements and shallow cores remain open. Our local pseudo-Hamiltonian, which incidentally can also speed up traditional local-density-functional calculations of very large scale, represents a promising tool for the quantum simulation of many molecular and solid-state systems, and a good starting point for further developments.

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## Table captions

Table I

The parameters of the function $a(r) = a_{\rm o} \exp[-(r/r_c)^k]$ for the atoms shown, in atomic units (see text).

Table II

The results of Bachelet *et al.* (1988), presented in Secs. 4 and 5. LSD: local-spin-density; NLPP: non-local pseudopotentials (Bachelet *et al.* 1982); PH: pseudo-Hamiltonian, Eq. (8) and Table I of this work (see Sec. 4). QMC: Green's Function Monte Carlo, release-node (Bachelet *et al.* 1989). The experimental values are from Weast (1988) for atoms and from Huber and Herzberg (1979) for molecules. All energies are in hartrees. E.A.: electron affinity; I.P.: ionization potential; $E_B$ : binding energy of the homo-nuclear diatomic molecule (no zero-point motion included) at the experimental bond separation. Shown in parentheses is the error bar: $0.118\ (3) = 0.118 \pm 0.003$.

Table III

The energy levels of the $Si^{3+}$. NLPP: nonlocal pseudopotentials (Bachelet *et al.* 1982); PH-1: $s, p$ pseudo-Hamiltonian (Bachelet *et al.* 1988, Secs. 4, 5 and Fig. 1, this work); PH-2: $s, p, d$ pseudo-Hamiltonian (Mitáš and Bachelet 1989, Sec. 6 and Fig. 4 of this work). Experimental values are from Bashkin and Stoner 1975.

## Figure captions

Figure 1

Silicon atom: the two kinetic-energy radial functions $a(r)$ and $b(r)$, and the atomic potential, $v(r)$, which characterize our local pseudo-Hamiltonian Eq. (8). Here we show the silicon pseudo-Hamiltonian which fixes $s$ and $p$ states exactly, and $d$ states only approximately: $a(r)$ has been parametrized and Eq. (13) solved only for $\ell = 0, 1$ (see Sec. 4 and Table I). Atomic units are used. A dashed line shows the coulombic tail $-4/r$.

Figure 2

Silicon logarithmic derivative of the local-density-functional radial wavefunction $\chi_\ell$ (evaluated at the covalent radius $R = 2.1$ a.u.) versus energy for $s$, $p$ and $d$ partial waves. The pseudo-Hamiltonian of Fig. 1 has been used. The dot marks the position of the eigenvalue $\varepsilon_\ell$. The solid lines are calculated with the full Si atom while the dashed lines are with the Si PH (see Eq. (8), Sec. 4 and Table I).

Figure 3

The energy of the $Si_2$ versus bond length as computed with QMC-PH (symbols with error bars, Bachelet *et al.* (1988), pseudo-Hamiltonian of Fig. 1), and with the full-core CI method (dots, McClean 1984). The local-spin-density full-core result is shown as a diamond (Jones 1985, 1987). The experimental binding energy and equilibrium bond length are $E_o$ and $R_o$ respectively (Weast 1988).

Figure 4

Silicon atom: the two kinetic-energy radial functions $a(r)$ (solid line) and $b(r)$ (dash-dotted), and the atomic potential, $v(r)$ (dashed), which characterize our local pseudo-Hamiltonian Eq. (8). Here we show the silicon pseudo-Hamiltonian which fixes $s$ and $p$ and $d$ states exactly, obtained by Mitáš and Bachelet (1989) by a simulated-annealing technique (see Sec. 6). Atomic units are used. Here, unlike Fig.1, the coulombic tail $-4/r$ is indicated by a dotted line.

Figure 5

The radial wavefunctions $\chi_\ell(r) = rR_\ell(r)$ which correspond to the bound state of the pseudo-Hamiltonian shown in Fig. 4 for $\ell = 0, 1, 2$. Atomic units are used.

**Table I**

| atom | $a_o$ | $r_c$ | $k$ |
|---|---|---|---|
| Na | 0. | | |
| Mg | -0.15 | 1.00 | 4 |
| Si | -0.74 | 1.30 | 4 |
| Cl | -0.80 | 1.10 | 6 |

**Table II**

| Sodium Z=11 | $E.A.$ | 1 I.P. | 2 I.P. | 3 I.P. | $E_B$ |
|---|---|---|---|---|---|
| full core LSD | | 0.1974 | | | - |
| NLPP + LSD | | 0.1932 | | | 0.0334 [a] |
| PH + LSD | | 0.1932 | | | - |
| PH + QMC | 0.0204 (7) | 0.1951 (1) | | | 0.0310 (6) |
| experiment | 0.0201 | 0.1889 | | | 0.0269 |
| Magnesium Z=12 | | | | | |
| full core LSD | | 0.2874 | 0.5635 | | 0.0043 [b] |
| NLPP + LSD | | 0.2804 | 0.5535 | | - |
| PH + LSD | | 0.2804 | 0.5536 | | - |
| PH + QMC | not stable | 0.2849 (3) | 0.5585 (2) | | 0.0015 (7) |
| experiment | not stable | 0.2810 | 0.5525 | | 0.00196 |
| Silicon Z=14 | | | | | |
| full core LSD | | 0.3027 | 0.5996 | 1.2339 | 0.1470 [b] |
| NLPP + LSD | | 0.3034 | 0.5993 | 1.2212 | - |
| PH + LSD | | 0.3034 | 0.5989 | 1.2205 | - |
| PH + QMC | 0.051 (1) | 0.301 (1) | 0.6057 (7) | 1.2356 (5) | 0.118 (3) |
| experiment | 0.0509 | 0.2995 | 0.6007 | 1.2308 | 0.119 (4) |
| Chlorine Z=17 | | | | | |
| full core LSD | | 0.4888 | 0.8819 | 1.4522 | - |
| NLPP + LSD | | 0.4849 | 0.8750 | 1.4537 | - |
| PH + LSD | | 0.4842 | 0.8720 | 1.4487 | - |
| PH + QMC | 0.138 (4) | 0.475 (4) | 0.878 (3) | 1.461 (3) | 0.08 (1)b |
| experiment | 0.1329 | 0.4765 | 0.8750 | 1.4556 | 0.0924 |

*a*: Martins *et al.* 1985

*b*: Jones 1985, 1987

**Table III**

| | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s |
|---|---|---|---|---|---|---|---|---|
| NLPP | -1.659 | -1.341 | -0.936 | -0.781 | -0.672 | -0.522 | -0.501 | -0.454 |
| PH-1 | -1.664 | -1.347 | -0.851 | -0.848 | -0.710 | -0.494 | -0.496 | -0.524 |
| PH-2 | -1.659 | -1.338 | -0.933 | -0.766 | -0.661 | -0.519 | -0.518 | -0.443 |
| Exper. | -1.659 | -1.333 | -0.928 | -0.775 | -0.664 | -0.520 | -0.501 | -0.450 |