Novel Pseudo-Hamiltonian for Quantum Monte Carlo Simulations

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Nonlocal potentials based on angular-momentum projectile operators can be transformed into local, yet angular-momentum–dependent, pseudo-Hamiltonians by modifying the kinetic energy operator. Ionic pseudo-Hamiltonians of this type can replace core electrons in atomic calculations. Their use in Green's-function Monte Carlo simulations gives accurate electron affinities, ionization, and binding energies for second-row atoms and diatomic molecules. This opens the way to quantum simulations of many condensed-matter systems.

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Quantum simulations, successful for simple systems,[1] remain difficult for atoms with core electrons. 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.[2] The standard solution—the replacement of core electrons with a pseudopotential—is not of help in this case: Accurate pseudopotentials are nonlocal (they contain angular-momentum projection operators),[3] which is in conflict with key aspects of quantum simulations. What we show here is that modern nonlocal pseudopotentials can be recast in terms of a modified kinetic energy operator which is, instead, local, and lends itself to an easy and successful use in quantum simulations.

In the study of an N-electron system the main limitation of the Green's-function Monte Carlo[4] method arises from the need to keep the Green's function

$$G(R,R';\Delta t)=\Psi(R)\Psi(R')^{-1} \times\langle R|\exp[-\Delta t(H-E_T)]|R'\rangle \quad (1)$$

non-negative, so that it can be sampled by a probability distribution.[5,6] In Eq. (1) Ψ is a trial wave function, R is a set of $3N$ electron coordinates, H is the Hamiltonian, E_T is a trial energy, and Δt is a small (imaginary) time step. This Green's function is used to project out the ground-state component of a trial function. The projection is implemented with branching random walks.[1]

For fermion systems the Green's function Eq. (1) has always negative pieces: Any fermionic wave function will change sign whenever two electrons with the same spin exchange. More generally, many-fermion wave functions show a complicated nodal structure separating regions of alternating sign. However, if one knew from the very beginning where the nodes of the exact ground-state wave functions were, one could then separately apply the Green's-function Monte Carlo method to each region of space, bounded by nodal surfaces, where the wave function does not change its sign. This can be approximately obtained by forcing the nodes of the sought, exact ground-state wave function, to be coincident with those of a reliable trial wave function Ψ: Then one always deals with non-negative Green's functions (fixed-node approximation).[1] If the Hamiltonian in Eq. (1) is local, one finds that in this approximation only the position of the nodes is important, not the values of Ψ anywhere else; and also that the estimated ground-state energy $E_{\rm FN}$ is variational: $E_{\rm FN}-E_0$ vanishes quadratically as the nodes of the trial function approach the nodes of the exact wave function and $E_{\rm FN}\geq E_0$ (if E_0 is the exact ground-state energy).[7] It can be further shown[8] that the most general form of a local Hamiltonian for which G is non-negative is

$$H=V(R)+\sum_{\alpha,\beta}p_\alpha g_{\alpha\beta}(R)p_\beta\,, \quad (2)$$

where the tensor $g_{\alpha\beta}=\partial^2 H/\partial p_\alpha\partial p_\beta$ is positive definite; i.e., the Hamiltonian contains momentum operators at most to the second power, and is bounded below. Only with such a Hamiltonian will all of the advantages of the fixed-node approximation exist. With this "pseudo-Hamiltonian" the electronic mass depends on position and direction.[8]

Let us see what the above requirements imply for pseudoatoms. Starting from Eq. (2) we simplify further and suppose that the pseudo-Hamiltonian for a collection of atoms has the same structure as the full Hamiltonian:

$$H=\sum_{i<j}\frac{1}{r_{ij}}-\tfrac{1}{2}\sum_i\nabla_i^2+\sum_{i,I}h_I(r_{iI})\,. \quad (3)$$

Atomic units are used throughout this paper; i and j refer to electrons and I to ions. Then the most general[8,9] atomic pseudo-Hamiltonian with these properties (and spherical symmetry) is

$$h(r)=-\tfrac{1}{2}\nabla a(r)\nabla+\frac{b(r)\mathbf{L}^2}{2r^2}+v(r)\,, \quad (4)$$

where $a(r)$, $b(r)$, and $v(r)$ are radial functions, and $\mathbf{L}^2$ is the angular-momentum operator. For $g_{\alpha\beta}$ to be positive definite (or H bounded below) we must require

$$a(r)>-1,\quad a(r)+b(r)>-1\,. \quad (5)$$

Outside the core of an atom, on physical grounds, we see that a and b must vanish and $v=-Z_v/r$ (Z_v is the valence charge).

With a pseudo-Hamiltonian of the form just shown we now try to optimally replace a full-core atom with a pseudo (valence only) atom which will be more easily treated by quantum Monte Carlo methods. Let us first see which properties are desirable for such a pseudo system. Outside the core, the ideal pseudoatom should reproduce the behavior of the true, full-core atom in a wide variety of chemical situations: not only for a given configuration of valence electrons (e.g., the ground-state isolated atom), but also for excited atomic configurations and within molecular or solid-state environments. This essential property of pseudo-Hamiltonians is often called *transferability*. Hamann, Schlüter, and Chiang[3] have shown that, whenever the many-electron problem is reduced to a set of self-consistent single-particle equations, for example, in local-density-functional or Hartree-Fock theory, optimum *transferability* is obtained by norm-conserving pseudopotentials.[3] The price to be paid is that these potentials contain projection operators of the angular momentum which are nonlocal. The Hamiltonian for a collection of such pseudoatoms is

$$H=\sum_{i<j}\frac{1}{r_{ij}}-\tfrac{1}{2}\sum_i\nabla_i^2+\sum_{i,I}\sum_l v_l(r_{iI})\sum_m\hat{P}_{lm}(\Omega_{iI}), \quad (6)$$

where $\hat{P}_{lm}$ is the angular-momentum projection operator, Ω_{iI} is the angular variable, and $v_l(r)$ are l-dependent radial functions; the other symbols have the same meaning as in Eq. (3). We now show that our pseudo-Hamiltonian, Eqs. (3) and (4), is, because of its angular-momentum dependence, able to reproduce the action of nonlocal norm-conserving pseudopotentials,[10] Eq. (6), in the relevant energy region. This can be immediately seen in a single-particle theory like local-density-functional theory. Here the three functions a, b, and v, which define the new pseudo-Hamiltonian, Eqs. (3) and (4), can be determined by requiring that its three lowest eigenfunctions and eigenvalues $\chi_l(r)$ and ϵ_l, for $l=0,1,2$, be *identical* to those of Eq. (6).[3,10] Subtracting the corresponding radial Schrödinger equations, one gets for $l=0,1,2$ a system of three equations

$$\left[-a\frac{d^2}{dr^2}+(a+b)\frac{l(l+1)}{r^2}-\frac{da}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)+2(v-v_l)\right]\chi_l=0 \quad (7)$$

for the three unknown functions a, b, and v. For a given pseudopotential $v_l(r)$ the three unknowns are thus uniquely determined. The system is solved by integrating a first-order differential equation for a, and then obtaining b and v in terms of a, da/dr, and combinations of (known) pseudopotentials and wave functions. From Eq. (7) we easily see that a, b, and v automatically recover the correct physical behavior outside the core ($a\to 0$, $b\to 0$, and $v\to -Z_v/r$), which also ensures that the new pseudo-Hamiltonian enjoys the same *transferability* as the original nonlocal pseudopotentials.

There is one question left: Do the a and b functions thus obtained satisfy the conditions of Eq. (5)? Unfortunately it turns out that they do not for many atoms and common types of norm-conserving pseudopotentials.[3,10] However, for many atoms which form s-p bonded systems, an exact reproduction of s and p orbitals is adequate: This holds for most atoms except transition metals and rare earths. With this in mind we restrict ourselves to two partial waves. This leaves the a function arbitrary inside the core and allows us to satisfy the conditions of Eq. (5). We choose the simple analytic form $a=a_0\exp[-(r/r_c)^k]$ which vanishes outside the core ($r>r_c$), and use Eq. (7) for $l=0,1$ to fix exactly only s and p orbitals. The three parameters a_0, r_c, and k (see Table I) are then chosen such that (i) the range of $a(r)$ roughly agrees with the extent of the atomic core, (ii) Eq. (5) is satisfied, and (iii) the d states are reasonably reproduced. The radial functions a, b, and v are shown in Fig. 1 for Si. The atomic excitations shown in Table II confirm that, with local-density-functional theory, the

TABLE I. The parameters of the function $a(r)=a_0\times\exp[-(r/r_c)^k]$ for the atoms shown, in atomic units (see text).

Atom	a_0	r_c	k
Na	0		
Mg	−0.15	1.00	4
Si	−0.74	1.30	4
Cl	−0.80	1.10	6

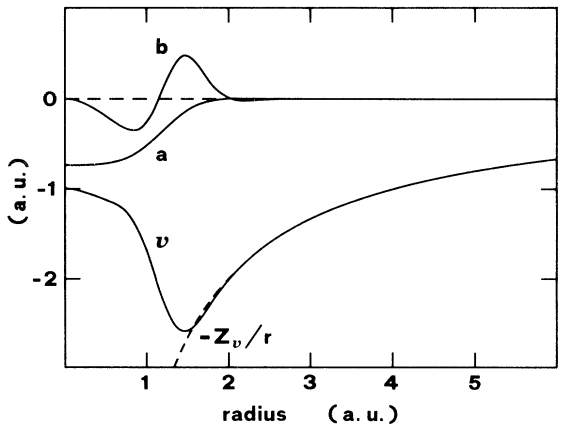

FIG. 1. The radial kinetic energy factors, $a(r)$ and $b(r)$, and the atomic potential, $v(r)$, for the silicon atom in atomic units. The dashed line shows the Coulombic tail.

TABLE II. The results of our calculations: LDF, local-density-functional theory (local spin density); NLPP, nonlocal pseudopotential (Ref. 10); PH, pseudo-Hamiltonian [Eq. (4) and Table I]; QMC, Green's function Monte Carlo, release node (see Ref. 6). The experimental values are from Ref. 11 for atoms and from Ref. 12 for molecules. All energies are in hartrees. E.A., electron affinity; I.P., ionization potential; E_B, binding energy of the homonuclear diatomic molecule (no zero-point motion included) at the experimental bond separation. Shown in parentheses is the error bar, e.g., $0.118(3)=0.118\pm0.003$.

	E.A.	1st I.P.	2nd I.P.	3rd I.P.	E_B
		Sodium $Z=11$			
Full-core LDF		0.1974			...
NLPP+LDF		0.1932			0.0334 [a]
PH+LDF		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 LDF		0.2874	0.5635		0.0043 [b]
NLPP+LDF		0.2804	0.5535		...
PH+LDF		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 LDF		0.3027	0.5996	1.2339	0.1470 [b]
NLPP+LDF		0.3034	0.5993	1.2212	...
PH+LDF		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 LDF		0.4888	0.8819	1.4522	...
NLPP+LDF		0.4849	0.8750	1.4537	...
PH+LDF		0.4842	0.8720	1.4487	...
PH+QMC	0.138(4)	0.475(4)	0.878(3)	1.461(3)	0.08(1)
Experiment	0.1329	0.4765	0.8750	1.4556	0.0924

[a]Reference 13. [b]Reference 14.

new pseudo-Hamiltonian is of comparable quality and *transferability* as the original, nonlocal pseudopotential: Both reproduce the full-core LDF atom accurately in a variety of valence configurations.

It is very likely that the angular-momentum dependence is a general property of *transferable* pseudo-Hamiltonians and is needed in the exact many-body theory. Moreover, there are arguments to expect that our ionic pseudo-Hamiltonian, defined and tested within local-density-functional theory, describes well the *physical ion.*[15] That encourages us to use it for quantum Monte Carlo simulations of valence electrons. All we need is a simple generalization of the diffusion Monte Carlo algorithm[1] and the same trial function employed in other quantum Monte Carlo calculations.[1,4] Such trial functions work 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 Monte Carlo, fixed-node diffusion Monte Carlo, and release-node[6] Monte Carlo calculations have been performed on the atoms and molecules shown in Table II. The calculations shown took between 1 min of CRAY time (for Na) to 2 h (for Cl_2).

The accuracy of our pseudo-Hamiltonian varies. The electron affinities are in perfect agreement with experiment[11] to the accuracy shown (which varies from 0.7 millihartree for Na to 4 millihartree 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 quantum Monte Carlo error bar by 6 and 4 millihartree, respectively. The homonuclear diatomic binding energies are in excellent agreement with experiment[12] 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 in Ref. 16 for atoms with significant core-valence overlap.

In conclusion, we have shown how to transform a class of nonlocal pseudopotentials into a local angular-momentum–dependent, pseudo-Hamiltonian. By this we could successfully eliminate core electrons from *s-p* systems and perform quantum Monte Carlo simulations for their valence electrons. Further refinements of the method are of course possible; a satisfactory description

of (strongly nonlocal) first-row elements and transition metals is desirable, and is likely to require stronger pseudopotentials inside the core.[17] The results for *s-p* atoms and molecules, however, already show the feasibility and the importance of an accurate description of valence electrons, beyond single-particle approximations: Our calculated electron affinities and molecular binding energies compare very favorably with the experiment, unlike those predicted by local-density-functional or Hartree-Fock theories.[18] It is finally interesting to observe the pseudo-Hamiltonians derived from local-density-functional atoms, as previously argued,[15] seem to give a good representation of the *physical ion*: Our results confirm that the core-valence interaction may be reasonably represented within single-particle approximations, while the exact description of the valence-valence interaction remains of key importance for a more accurate description of condensed-matter systems. Our local pseudo-Hamiltonian offers a promising tool for such an exact study.

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[6]Actually it is possible to treat Green's functions with negative pieces: See Ref. 5 and D. M. Ceperley and B. J. Alder, J. Chem. Phys. **81**, 5833 (1984); this method (often called "release node") can be applied to atoms and molecules, but is not appropriate for larger systems: The statistical error grows rapidly with the number of electrons. For this reason it is generally preferable to deal with non-negative Green's functions.

[7]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 electronic systems (see Ref. 1).

[8]A detailed derivation will be given elsewhere. See also N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford Univ. Press, New York, 1965).

[9]It is possible in fact to make the local potential a more general function of R in Eqs. (2) and (3), for example, by modifying the electron-electron interaction inside the core to mimic the effect of core polarizability. We do not consider such a possibility here. Other authors [M. M. Hurley and P. A. Christiansen, J. Chem. Phys. **86**, 1069 (1987); B. L. Hammond, P. J. Reynolds, and W. A. Lester, Jr., *ibid.* **87**, 1130 1987)] have made a local potential by projecting a nonlocal "shape-consistent" pseudopotential onto a Hartree-Fock trial function. This approach, in principle, requires that the trial function be accurate everywhere, not just at the node.

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[18]Local-density-functional and Hartree-Fock theories predict negative ions which either are not bound at all or show unreasonable electron affinities [see J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981)]; local-density-functional theory has a marked tendency to overbind *s-p* bonded molecules (see Refs. 13 and 14).