

## Newtonian and fluid-dynamical viewpoint of pseudopotentials

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**Abstract.** A generalized time-dependent pseudopotential is defined. Analogue of the Newtonian equation is derived for stationary states and pseudoforces are physically interpreted. Physical points are also made from the analogous equation of continuity and the Euler equations.

**Keywords.** Pseudopotential; pseudoforces; fluid dynamics; Euler equation.

### 1. Introduction

Recent years have seen an upsurge in the use of pseudopotentials in valence electron theories and calculations (Cohen and Heine 1961; Szasz 1968; Kahn and Goddard 1972; Ewig and Van Wazer 1975; Ewig *et al* 1977; Datta *et al* 1978; Datta 1980). Briefly speaking, suppose that the study of a constrained function  $\psi_v$  is to be carried out with an unmodified hamiltonian  $\mathcal{F}$ ,

$$i\hbar \frac{\partial}{\partial t} \psi_v(r, t) = \mathcal{F} \psi_v(r, t),$$

$$\mathcal{F} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r, t), \quad (1)$$

such that a set of stationary functions  $\{\psi_c\}$  with eigenvalues  $\{\epsilon_c\}$  is available,  $\langle \psi_v | \mathcal{F} | \psi_v \rangle > \epsilon_c$  for all  $\psi_c$ , and  $\psi_v$  is orthogonant to all  $\psi_c$ . It is now required to replace this treatment by one using the unconstrained pseudofunction  $\chi_v(r, t)$  and a hamiltonian modified by a pseudopotential ( $\mathcal{F} + V^{\text{GPP}}(t)$ ).  $\chi_v$  is chosen such that

$$(1 - \hat{P}) \chi_v = \psi_v, \quad (2)$$

where use has been made of the *core* projection operator  $\hat{P} = \sum_c |\mathbf{c}\rangle \langle \mathbf{c}|$ . Combining (1) and (2) one obtains

$$i\hbar \langle \chi_v | 1 - \hat{P} | \dot{\chi}_v \rangle = \langle \chi_v | (1 - \hat{P}) \mathcal{F} (1 - \hat{P}) | \chi_v \rangle. \quad (3)$$

Independent variation of  $\chi_v^*$  yields the result

$$i\hbar |\dot{\chi}_v\rangle = [\mathcal{F} + V^{\text{GPP}}(t)] |\chi_v\rangle, \quad (4)$$

where 
$$V^{\text{GPP}}(t) = -\hat{P}\mathcal{F} - \mathcal{F}\hat{P} + \hat{P}\mathcal{F}\hat{P} + i\hbar \hat{P}|\dot{\chi}_v\rangle / |\chi_v\rangle. \quad (5)$$

We define  $V^{\text{GPP}}(t)$  as the generalized time-dependent pseudo-potential.

In the specific case that  $\psi_v$  corresponds to a stationary state  $\psi_v(r, t) = \psi_v(r, 0) \exp(-i t \epsilon_v / \hbar)$ , with  $\epsilon_v > \epsilon_c$ ,  $\chi_v$  is the unconstrained (stationary) eigenfunction,

$$\chi_v(r, t) = \chi_v(r, 0) \exp(-i/\hbar t \epsilon_v)$$

of the operator  $(\mathcal{F} + V^{\text{GPP}})$  where  $V^{\text{GPP}}$  is the generalized time-independent pseudo-potential

$$V^{\text{GPP}} = -\hat{P}\mathcal{F} - \mathcal{F}\hat{P} + \hat{P}\mathcal{F}\hat{P} + \epsilon_v \hat{P}, \quad (6)$$

a result derived by Weeks *et al* (1969). In case  $\psi_c$ 's are all eigenfunctions of  $\mathcal{F}$ , the time-dependent and time-independent pseudopotentials reduce to the Phillips-Kleinman (1959) form

$$V^{\text{PK}}(t) = \sum_c |c\rangle \langle c| (-\epsilon_c + i\hbar |\dot{\chi}_v\rangle / |\chi_v\rangle), \quad (7a)$$

and 
$$V^{\text{PK}} = \sum_c |c\rangle \langle c| (\epsilon_v - \epsilon_c). \quad (7b)$$

Some of the well-known features, *e.g.*, that the time-independent pseudopotentials  $V^{\text{GPP}}$  or  $V^{\text{PK}}$  add a non-local, hermitian and repulsive contribution to the net potential, have been well illustrated by Weeks *et al* (1969). It is required here to investigate the analogue of the Newtonian equation of motion and the fluid-dynamical viewpoints corresponding to the pseudopotentials which hopefully will elaborate a few physical pictures.

## 2. Analogue of the Newtonian equation for stationary states

The Heisenberg equation of motion can be used to determine the force due to the unmodified hamiltonian,

$$\mathbf{F} = -i\hbar \dot{\nabla} = -[\nabla, \mathcal{F}] = -(\nabla V), \quad (8a)$$

containing all the contributions from electron-nuclear and electron-electron interactions in a chemical system, and similarly the analogous Newtonian force generated by the pseudopotentials

$$\begin{aligned} \mathbf{F}^{\text{GPP}} &= -(\nabla V^{\text{GPP}}) \\ &= -\hat{P}\mathbf{F} - \mathbf{F}\hat{P} + \hat{P}\mathbf{F}\hat{P} + (\nabla\hat{P})\mathcal{F}(1 - \hat{P}) + (1 - \hat{P})\mathcal{F}(\nabla\hat{P}) \\ &\quad - \epsilon_v(\nabla\hat{P}). \end{aligned} \quad (8b)$$

Interpretation of (8b) is sought in the following two ways.

If the core orbitals  $\psi_c$ 's are eigenfunctions of  $\mathcal{F}$ ,  $\mathbf{F}^{\text{GPP}}$  reduces to the Phillips-Kleinman force

$$\mathbf{F}^{\text{PK}} = -\mathbf{F}\hat{P} - \sum_c (\epsilon_v - \epsilon_c) (\nabla P_c), \quad (8c)$$

which is hermitian and non-local. We note that (i) *the first term on the right hand side of (8c) describes the subtraction of more attractive forces due to the charge distribution in the core part of the pseudofunction, contributing to a repulsive character as mentioned by Weeks et al (1969) but not explicitly shown by them; the second term describes the contribution due to the spatial variation of the core projection.*

Another way of interpreting (8b) is to make a further use of the Heisenberg equation of motion

$$\nabla = \frac{\mu}{\hbar^2} [\mathbf{r}, F],$$

leading to the result (for a complete basis)

$$\mathbf{F}^{\text{GPP}} = \mu \sum_c^{\text{core}} \sum_i^{\text{core+valence}} \omega_{vc} \omega_{ic} \{ \mathbf{r}_{ic} | i \rangle \langle c | + \text{c.c.} \} \quad (8d)$$

where  $\mathbf{r}_{ic} = \langle i | \mathbf{r} | c \rangle$  and  $\omega_{ij} = (\epsilon_i - \epsilon_j) / \hbar$ . Thus (ii) *the pseudoforce describes a weighted projection of the amplitudes of transitions between the core and core or valence orbitals in the electric dipolar form.* This resembles a weighted change in a central ( $m\omega^2 R$ ) type of a force faced by the charge distribution in transition from the core space to the sum of core and valence spaces. Equivalently one may view its effect as a partial squeezing of the core part of the pseudoorbital into the pure valence space.

In passing one notes that there is no counterpart of the gradients of the quantum potential (Bohm 1952) in the force operator as given by (8a), an item that is exhibited in the fluid-dynamical aspects (in the Schrödinger picture) of the system.

### 3. Fluid-dynamical viewpoint

Multiplying both sides of (4) by  $\chi_v^*$  and making a complex conjugate one obtains a pair of initial equations. Subtraction between them results into the equation of continuity

$$\left[ \frac{\partial}{\partial t} - \frac{2}{\hbar} \text{Im}(V) - \frac{2}{\hbar} \text{Im}(\chi_v^* V^{GPP}(t) | \chi_v \rangle / \tilde{\rho}) \right] \tilde{\rho} = -\nabla \cdot \tilde{\mathcal{J}}, \quad (9a)$$

where  $\rho$ , the pseudo-density field and  $\tilde{\mathcal{J}}$ , the pseudo-probability current are given by

$$\tilde{\rho} = \chi_v^* \chi_v, \quad (9b)$$

$$\text{and } \tilde{\mathcal{J}} = (-i\hbar/2\mu)(\chi_v^* (\nabla \chi_v) - (\nabla \chi_v^*) \chi_v). \quad (9c)$$

A general pseudo-velocity field  $\tilde{\mathbf{v}}$  can be defined such that

$$\tilde{\mathcal{J}} = \tilde{\rho} \tilde{\mathbf{v}}, \quad (9d)$$

$$\text{and correspondingly, } \tilde{\mathbf{v}} = (-i\hbar/2\mu) \nabla \ln(\chi_v/\chi_v^*). \quad (9e)$$

Equations (9) are well compared with the equation of continuity for a Schrödinger fluid (Wong 1976).

Instead of subtraction, if one carries out an addition of the initial conjugate equations, one obtains the analogue of the Newtonian equation

$$\mu \dot{\tilde{\mathbf{v}}} = -\nabla \left[ \text{Re} \left\{ \frac{-\hbar^2 \nabla^2 \chi_v}{2\mu \chi_v} \right\} + \text{Re}\{V\} + \text{Re}\{\chi_v^* V^{GPP}(t) | \chi_v \rangle / \tilde{\rho}\} \right], \quad (10)$$

where the first term on the right side corresponds to the quantum potential (Bohm 1952), the second term to the electron-nuclear and electron-electron interactions, and the third one to the pseudopotentials.

That the imaginary part of the potentials contribute to the equation of continuity is a general trend, for the formal solution of (4)

$$\chi_v(t) = \exp \left\{ -\frac{it}{\hbar} (\mathcal{F} + V^{GPP}(t)) \right\} \chi_v(0), \quad (11a)$$

admits the result

$$\dot{\tilde{\rho}} - \frac{2}{\hbar} \text{Im} \left\{ V + \chi_v^* V^{GPP}(t) | \chi_v \rangle / \tilde{\rho} \right\} \tilde{\rho} = -\frac{i}{\hbar} [\tilde{\rho}, \text{Re}\{\mathcal{F} + V^{GPP}(t)\}], \quad (11b)$$

as compared to (9a). We note that:

(iii) *the effect of the imaginary components of potentials in the equation of continuity is to cancel the imaginary part of the pseudohamiltonian from appearing in the*

commutator of (11b) and again, comparison with the right side of (9a) illustrates that the analogue of the Newtonian equation involving the velocity field contains the contribution from only real part of the pseudohamiltonian.

In order to give a complete description of the fluid-dynamics, a more appropriate equation will be the analogue of Euler equation instead of the Newtonian one. Putting  $\chi_v$  as

$$\chi_v = \tilde{\phi}_v \exp \left\{ \frac{i\mu}{\hbar} \tilde{S}(r, t) - i\Omega(t) \right\}, \quad (12)$$

in the initial conjugate equations, after a little bookkeeping and making use of the equation of continuity, one obtains the analogue of Euler equations

$$\begin{aligned} \mu \left[ \frac{\partial}{\partial t} - \frac{2}{\hbar} \frac{\text{Im}(V)\tilde{\phi}}{\tilde{\phi}} - \frac{2}{\hbar} \text{Im}(\chi_v^* V_{(t)}^{GPP} | \chi_v \rangle / \tilde{\rho}) \right] \tilde{\mathcal{J}} \\ + \sum_j \nabla_j (\mu \tilde{\phi}^2 \nabla \tilde{S} \nabla_j \tilde{S} + \sum_i \hat{i} p_{ij}^{(q)}) \\ = - \tilde{\phi}^2 \nabla \{ \tilde{\phi}^{-1} \text{Re}(V)\tilde{\phi} + \text{Re}(\chi_v^* V_{(t)}^{GPP} | \chi_v \rangle / \tilde{\rho}) \}, \end{aligned} \quad (13)$$

where on the right hand side the force density arises out of the gradient of the real part of interactions and pseudopotentials; the terms  $p_{ij}^{(q)}$  are stress tensors describing the pseudo-shear stresses (off-diagonal) and quantum pressures (diagonal)

$$p_{ij}^{(q)} = - \frac{\hbar^2}{4\mu} \nabla^2 \tilde{\phi}^2 \delta_{ij} + \frac{\hbar^2}{\mu} \nabla_i \tilde{\phi} \nabla_j \tilde{\phi}, \quad (14a)$$

comparable to the expressions given by Wong (1976) for exact functions. The pseudo-probability density and pseudo-probability current are now given by

$$\tilde{\rho} = \tilde{\phi}^2 \quad (14b)$$

$$\text{and } \tilde{\mathcal{J}} = \tilde{\phi}^2 \nabla \tilde{S}. \quad (14c)$$

For stationary pseudofunctions, the stresses must balance with the right side of (13) and we note that (iv) *the effect of the pseudopotentials is to counterbalance exactly the difference between pseudo-shear stresses and negative gradient of the real part of interactions, so that a stationary state of the pseudohamiltonian may be generated.*

For the single particle case,  $V$  can be considered as a real, scalar potential. For a many-body system,  $V$  will also contain the direct and exchange two-particle interaction terms, and the latter type of terms can contribute to the imaginary portion in  $V$ . Following Wong (1976), the Euler equation may be readily generalized for the many-body system in time-dependent Hartree-Fock Scheme, although no other significant information on pseudopotentials seems to be achieved.

#### 4. Discussion

Here we indicate some of the possible uses of the previous analysis. For this purpose two different forms of the time dependence of the pseudofunction are considered in the tight-binding approximation for a model crystal:—

$$(i) \quad \chi_v(r, t) = \tilde{\phi}_v(r) \exp [i(\mathbf{k} \cdot \mathbf{r} - \omega_k t)]$$

where  $\tilde{\phi}_v(r) \sim \sum_s c_s \psi_{v,s}(r)$  are linear combinations of the basic valence functions, corresponding to the exact single particle valence function  $\Phi_v$ ,

$$\text{and (ii) } \chi_v(r, t) = \Phi_v(r, 0) \exp(-it\epsilon_v/\hbar) + \exp(-it\epsilon_c/\hbar) \sum_s g(s, t) \psi_{c,s}(r, 0);$$

in this form  $\chi_v(r, t)$  may as well be compared to an intermediate excitation; the summations are over lattice sites.

From (9e) one obtains different expressions of the velocity field for different choices. For choice (i),  $\tilde{\mathbf{v}} = \hbar\mathbf{k}/\mu$  so that ( $\mathbf{k}=0$ ) function becomes a representative for the stationary states. For choice (ii), in case the coefficient is independent of the lattice sites,  $\chi_v$  retains crystal symmetry. The velocity field  $\tilde{\mathbf{v}}$  is not necessarily vanishing; for example, if  $g(s, t) = \text{constant}$ ,  $\tilde{\mathbf{v}}$  fluctuates periodically around the mean, vanishing mean value, with a time period  $h/(\epsilon_v - \epsilon_c)$ ; if  $g(s, t) = \gamma \exp(-\kappa t)$  where  $\gamma$  and  $\kappa$  are constants,  $\chi_v$  relaxes back to  $\psi_v$  with increasing time; for small  $\gamma$ ,  $\tilde{\mathbf{v}}$  fluctuates periodically around its mean exponential decay with the same time period. In case  $g(s, t)$  is chosen as a judicious function of the lattice points, a net propagation of the intermediate excitation described by  $\chi_v$  can be obtained. The velocity field is, in general, coordinate-dependent.

An experimental parameter for the second choice is hence, e.g. diffusion coefficient  $D(\omega)$  expressed as the noise spectrum of the momentum autocorrelation function

$$D(\omega) = \mu^{-2} \int_0^{\infty} dt \exp(-i\omega t) \langle p(t) \cdot p(0) \rangle_{\text{ensemble}}$$

For choice (i), the macroscopic diffusion coefficient  $D(0)$  is purely imaginary and  $D(\omega)$  has poles at  $\omega = \omega_k$ . For choice (ii),  $D(\omega)$  can be calculated to be  $D(\omega) = D'(\omega) + iD''(\omega)$ , where the real part describes a diffusive process and the imaginary part represents a periodic one (wave-like fluctuations) with poles still at  $\omega = \omega_k$ . For example, for small  $\gamma$ , the macroscopic diffusion coefficient in atomic unit is given by

$$D'(0) = \gamma\kappa \left( \frac{1}{\kappa^2 + (\omega - \epsilon_v)^2} + \frac{1}{\kappa^2 + (\omega - \epsilon_c)^2} \right) \sum_s \int d\tau \nabla \Phi_v \cdot \nabla \psi_{c,s} \\ + \frac{2\gamma^2\kappa}{4\kappa^2 + (\omega - \epsilon_c)^2} \sum_{s,s'} \int d\tau \nabla \psi_{c,s} \cdot \nabla \psi_{c,s'}$$

These ideas may find applications in solid state physics and details of such applications will appear in a forthcoming publication.

The condition that stresses must balance the forces for a stationary state can reasonably be exploited to determine simple forms of the pseudovalence basis. For stationary states  $\tilde{\phi}_v = \Phi_v + \sum_s a_s \psi_{c,s}$  and (13) reduces to

$$-\frac{\hbar^2}{2\mu} \nabla_t \left( \frac{\nabla^2 \tilde{\phi}_v}{\tilde{\phi}_v} \right) = -\nabla_t V - \sum_s a_s (\epsilon_v - \epsilon_c) \nabla_t \left( \frac{\psi_{c,s}}{\tilde{\phi}_v} \right). \quad (15)$$

As an illustration we consider the *lowest* energy valence orbital for a *model* crystal system of simple cubic symmetry with spacing 3.0 atomic units. The choice of the GTO basis is described in table 1. The isolated atomic orbital energies are  $\epsilon_c = -2.47773$  and  $\epsilon_v = -0.19632$  hartree whereas the crystal orbital energies are  $\epsilon_c = -2.47779$  and  $\epsilon_v^{\text{lowest}} = -0.21401$  hartree (apart from the constant crystal potential), where for each individual unit a screening constant 2.0 has been employed. The 2s band width is 0.9645 eV. In case the valence basis can be described by a single gaussian  $\exp(-\tilde{\alpha} r^2)$ , near the origin of a unit cell, (15) reduces to

$$f(r) \equiv 24 \tilde{\alpha}^2 - \frac{1}{r} \frac{\partial V}{\partial r} - 6 \left( \sum_s \langle \psi_{c,s} | \psi_{v,o} \rangle \right) (\epsilon_v - \epsilon_c) \\ \otimes \sum_j d_j (\pi/2\tilde{\alpha})^{3/4} (\tilde{\alpha} - \alpha_j) \exp \{ (\tilde{\alpha} - \alpha_j) r^2 \} = 0,$$

where  $d_j$  and  $\alpha_j$  are the core gaussian coefficients and exponents as described in table 1. In figure 1 the function  $f(r)$  is plotted against  $r$  for various values of  $\tilde{\alpha}$ . The best  $\tilde{\alpha}$  obtained is 0.84, as compared to the valence basis in table 1 where the predo-

Table 1. Gaussian basis and results for model atom and crystal\*.

Orbital	1s	2s
Atomic orbital energy in atomic unit	-2.47773	-0.19632
Orbital exponents	orbital coefficients	
1s 2.47673	0.89786	-0.14629
1s 4.69873	0.11131	-0.01916
2s 0.38350	-0.00000	0.00377
2s 0.66055	0.00112	0.98653
2s 1.07000	-0.00214	0.16971
2s 1.63200	0.06884	-0.11021
Crystal orbital energy in atomic unit**	-2.47779	-0.21401†

\*Basis chosen corresponding to Li atom; assumed crystal of simple cubic symmetry with 3.0 atomic unit spacing.

\*\*Apart from the constant crystal field for the presence of other atoms.

†Corresponds to the lowest energy valence orbital in the 2s band (tight-binding approximation).

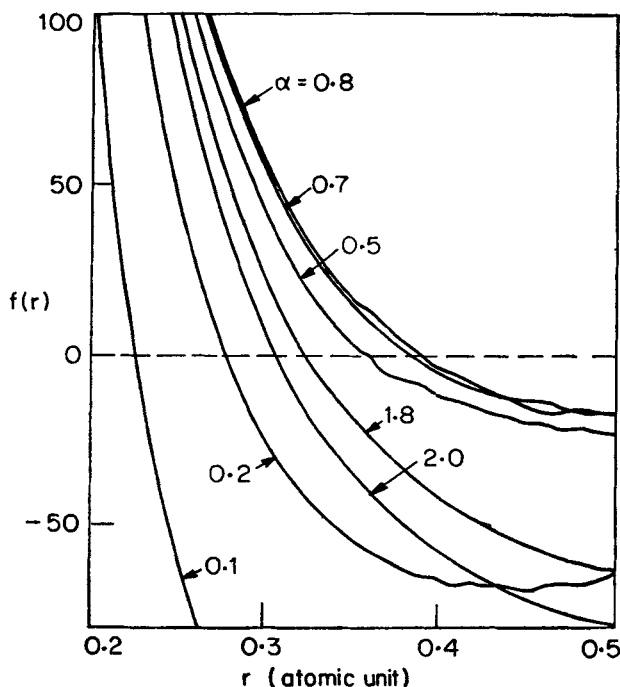


Figure 1. Test of single gaussians as basis for crystal pseudo-valence orbitals corresponding to stationary states.

minant gaussians are those with exponents 0.66055 and (1.07, 2.47673 and 1.632). The conclusion from figure 1 is that a single gaussian is an inadequate description for pseudovalence functions corresponding to the stationary states. A reasonable GTO basis can similarly be found starting with (15).

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