

DOUG'S ATOMIC PSP PACKAGE

Douglas C. Allan

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These typewritten notes were transcribed from the handwritten notes used by Doug Allan during early development of separable nonlocal pseudopotentials and norm-conserving pseudopotentials that laid part of the foundation for the OPIUM and ABINIT codes for pseudopotential generation and electronic structure calculations. See opium.sourceforge.net and www.abinit.org for more information.

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Given atomic Z , nlm 's, occupation numbers and initial guesses for eigenvalues, and various control parameters, can compute:

1. All electron result, storing core charge for program core calculations.
2. Non-norm conserving psp.
3. HSC psp.
4. "Extended" HSC psp.
5. Reading in one of above core potentials, will compute new configurations of occ number.

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Contents

1	The big picture	4
1.1	Atomic structure with all electrons (AE)	4
1.2	Soft core psp	4
1.3	Norm-conserving psp (HSC)	5
1.4	Extended norm cons psp	6
1.5	Unscreening and the core potential	6
2	Mathematical details	6
2.1	All electron HFS-SCF	6
2.1.1	General equations of atomic problem	6
2.1.2	Exchange and correlation (excorr)	12
2.2	Pseudopotentials (all soft core)	19
2.2.1	Non-norm conserving	19
2.2.2	Norm-conserving	20
2.2.3	Extended norm conserving	24
2.3	Frozen core calculations	29
3	Numerical details	33
3.1	Coordinate derivatives	39
3.2	Length scale derivatives	41

1 The big picture

1.1 Atomic structure with all electrons (AE)

We initially aim to solve a one-electron Schrödinger equation derived variationally from a local density functional approximation to the atomic total energy. This amounts to solving for eigenfunction $\psi_i(\vec{r})$ moving in some self-consistent field (SCF), $V(\vec{r})$

$$(-\nabla^2 + V(\vec{r})) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (\text{I-1})$$

(Rydberg energy units)

We ignore angular variations and use a spherically averaged $V(r)$, allowing the usual separation into angular and radial equations. We are ignoring particular orbital configurations of open shells by averaging over occupation of various m in ψ_{nlm} .

Using $\psi_{nlm} = Y_{lm}(\theta, \phi) \cdot \hat{R}_{nl}(r)$

and $R_{nl}(r) \equiv r \cdot \hat{R}_{nl}(r)$

the resulting radial equation is

$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} \right) R_{nl}(r) = \varepsilon_{nl} R_{nl}(r) \quad (\text{I-2})$$

The details of obtaining $V(r)$ and solving for the spectrum of core and valence ε_{nl} and $R_{nl}(r)$ are presented later.

For any given all electron (AE) SCF calculation, some fixed set of occupation numbers w_{nl} are provided. These tell how many electrons occupy orbital R_{nl} , which is needed for building up the charge density from the $\{R_{nl}\}$. Each AE calculation for a given Z will have a different spectrum of eigenvalues $\{\varepsilon_{nl}\}$ resulting from particular choices of $\{w_{nl}\}$

1.2 Soft core psp

“Atomic core” = nucleus + core electrons

The psp $V_{\text{ps}}(r)$ mimics the influence of the atomic core on the valence states. A nonlocal psp:

$$V_{\text{ps}}^{\text{NL}} = \sum_{\ell=0}^{\infty} V_{\text{ps}}^{\ell}(r) \cdot P_{\ell}$$

acts with different functional forms $V_{\text{ps}}^{\ell}(r)$ on different components of the angular momentum (P_{ℓ} is a projection operator onto angular momentum ℓ).

In some reference state (*i.e.* for some reference choice of $\{w_{nl}\}$, *e.g.* the ground state of the atom) the psp is designed to give the AE $V(r)$ outside of some chosen core radius r_{mc} , and to reproduce exactly the valence eigenvalue. A useful soft core psp form is that of HSC,

$$V_1(r) = V^{\text{AE}}(r) \left(1 - f\left(\frac{r}{r_c}\right) \right) + cf\left(\frac{r}{r_c}\right) \quad (\text{I-3})$$

where $f\left(\frac{r}{r_c}\right)$ is essentially a smoothed cutoff function which behaves like $1 - \Theta\left(\frac{r}{r_c}\right)$ for $\Theta = \text{step function}$.

BHS use $f\left(\frac{r}{r_c}\right) = e^{-\left(\frac{r}{r_c}\right)^{\lambda}}$, $\lambda \simeq 3.5$.

c is merely adjusted to reproduce the AE eigenvalue using $V_1(r)$ in place of $V(r)$. Since $V_1(r) \rightarrow c$ as $r \rightarrow 0$, it is evidently soft core. We have removed a $-2Z/r$ singularity which was present in $V(r)$.

Since $V_1(r) \rightarrow V(r)$ as $r \gg r_c$, the pseudoeigenfunction $w_1(r) \propto R_{nl}(r)$ but need not equal $R_{nl}(r)$ at $r \gg r_c$.

After normalization, $w_1(r)$ would be greater or less than $R(r)$ for $r > r_c$, depending on how $w_1(r)$ turns out for $r < r_c$. For this psp we have no control over the behavior of $w_1(r)$ inside $r < r_c$.

1.3 Norm-conserving psp (HSC)

To reproduce $R_{nl}(r)$ exactly outside the core ($r > r_c$) HSC chose to “cluge up” $w_1(r)$ inside $r < r_c$. Thus,

$$w_2(r) \equiv \gamma \left(w_1(r) + \delta r^{l+1} f\left(\frac{r}{r_c}\right) \right) \quad (\text{I-4})$$

where γ is adjusted to make

$$w_2(2r_m) = R_{nl}(2r_m) \quad \text{where } r_m \text{ is } r \text{ at which } R_{nl} \text{ has last max}$$

and δ ensures,

$$\int_0^\infty w_2^2(r) dr = 1$$

A final “norm conserving” psp is obtained from $w_2(r)$ by inverting the Schrödinger equation.

The advantages of the resulting potentials are discussed in references 1, 2, 4, and 9.

1.4 Extended norm cons psp

See reference 9.

1.5 Unscreening and the core potential

The pseudopotentials described above include screening by the valence electrons. The actual core or “ionic” psp used for applications other than trivially reproducing the reference configuration has the screening terms subtracted off. The Hartree and the exchange and correlation terms of $V(r)$ are computed using the pseudowavefunctions and subtracted off $V_{\text{ps}}(r)$, yielding $V_{\text{ps}}^{\text{core}}(r)$. Since the exchange-correlation (*excrr*) term varies with density as $\rho^{1/3}$, the approximation of subtracting off the *excrr* term commits an error by linearizing $\rho^{1/3}$. See reference 10 for a tractable scheme for avoiding this error. This becomes important when core and valence charge densities overlap much, or when *SPIN POLARIZED CALCULATIONS* are desired. After the frozen core error of the psp approximation, this linearization error is the largest remaining error (in my experience).

2 Mathematical details

2.1 All electron HFS-SCF

2.1.1 General equations of atomic problem

Consistently use Rydberg atomic units (also used by programs).

Density functional (Hohenberg and Kohn - see reference 4) ground state total energy variationally minimizes

$$E[\rho] = \int v(\vec{r})\rho(\vec{r})d^3r + F[\rho] \tag{II-1}$$

where $v(\vec{r})$ is the external potential; $-2Z/r$ for us.

Reformulate $F[\rho]$ as,

$$F[\rho] = \underbrace{\frac{1}{2} \int \frac{2\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r'}_{\text{H-C}^1} + \underbrace{T_0[\rho]}_{\text{KE}^2} + \underbrace{E_{\text{xc}}[\rho]}_{\text{EC}^3} \quad (\text{II-2})$$

Make a local approximation,

$$E_{\text{xc}}[\rho] \simeq \int \rho(\vec{r}) \varepsilon_{\text{xc}}(\rho(\vec{r})) d^3r \quad (\text{II-3})$$

where ε_{xc} is a function of ρ , parametrized in a variety of ways from calculations on electron gases.

To solve variationally,

$$E[\rho] = \int \left(\underbrace{v(\vec{r})}_{\frac{-2Z}{|\vec{r}|}} + \varepsilon_{\text{H}}(\vec{r}) + \varepsilon_{\text{xc}}(\rho(\vec{r})) \right) \rho(\vec{r}) d^3r + T_0[\rho] \quad (\text{II-4})$$

where

$$\varepsilon_{\text{H}}(\vec{r}) = \frac{1}{2} \int \frac{2\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' \quad (\text{II-5})$$

is the Hartree energy density. Take variations.

$$\delta E = \int \delta\rho(\vec{r}) \left\{ v(\vec{r}) + \frac{\delta(\rho\varepsilon_{\text{H}})}{\delta\rho} + \frac{\delta(\rho\varepsilon_{\text{xc}})}{\delta\rho} + \frac{\delta(T_0)}{\delta\rho} \right\} d^3r = 0 \quad (\text{II-6})$$

subject to

$$\int \rho(\vec{r}) d^3r = N$$

$$\begin{aligned} \frac{\delta(\rho\varepsilon_{\text{H}})}{\delta\rho} &= \varepsilon_{\text{H}}(\vec{r}) + \int \rho(\vec{r}') \frac{\delta\varepsilon_{\text{H}}(\vec{r}')}{\delta\rho(\vec{r})} d^3r' & \frac{\delta\varepsilon_{\text{H}}(\vec{r}')}{\delta\rho(\vec{r})} &= \frac{1}{|\vec{r}-\vec{r}'|} \\ &= \varepsilon_{\text{H}}(\vec{r}) + \int d^3r' \rho(\vec{r}') \frac{1}{|\vec{r}-\vec{r}'|} = 2\varepsilon_{\text{H}}(\vec{r}) \end{aligned}$$

¹ “Hartree” direct Coulomb interaction energy

² Kinetic Energy of a noninteracting electron gas of density $\rho(\vec{r})$

³ “Exchange-correlation” energy

$$\Rightarrow \mu_H(\vec{r}) = \frac{\delta}{\delta\rho(\vec{r})}(\rho\varepsilon_H) = 2\varepsilon_H(\vec{r}) \quad (\text{II-7})$$

For excorr,

$$\begin{aligned} \frac{\delta}{\delta\rho(r)}(\rho\varepsilon_{xc}) &= \varepsilon_{xc}(\rho(r)) + \int d^3r' \rho(r') \frac{\delta\varepsilon_{xc}\rho(r')}{\delta\rho(r)} \\ &= \varepsilon_{xc}\rho(r) + \rho(r) \frac{\partial\varepsilon_{xc}(\rho)}{\partial\rho}(r) \\ \Rightarrow \mu_{xc}(\vec{r}) &\equiv \frac{\delta}{\delta\rho(r)}(\rho\varepsilon_{xc}(\rho)) = \varepsilon_{xc}(\rho(r)) + \rho(r) \frac{\delta\varepsilon_{xc}(\rho)}{\delta\rho} \end{aligned} \quad (\text{II-8})$$

μ_{xc} can be evaluated given some choice of $\varepsilon_{xc}(\rho)$.

In terms of definition (II-7) and (II-8), we must solve

$$\int \delta\rho(r) \left(v(\vec{r}) + \mu_H(\vec{r}) + \mu_{xc}(\vec{r}) + \frac{\delta T_o}{\delta\rho(r)} \right) d^3r = 0 \text{ with } \int d^3r \rho(r) = N.$$

To obtain the correct $(\rho(r))$ we can solve the non-interacting system (kinetic energy (T_o) subject to a potential of the form

$$V(\vec{r}) = v(\vec{r}) + \mu_H(\vec{r}) + \mu_{xc}(\vec{r}) \quad (\text{II-9})$$

To implement $\int d^3r \rho(r) = N$, use $\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2$ (with $\int |\Psi_i(r)|^2 d^3r =$

1) and introduce Lagrange multipliers ε_i . Express variations in $\rho, \delta\rho(r)$, by $\delta\Psi_i^*(r)$ to obtain an unconstrained variational problem.

$$\frac{\delta}{\delta\psi_i^*} \left\{ E[\rho] - \varepsilon_i \int d^3r \rho(r) \right\} = 0 \quad (\text{II-10})$$

The resulting variationally derived equation is the desired Schrödinger equation

$$\boxed{[-\nabla^2 + v(\vec{r}) + \mu_H(\vec{r}) + \mu_{XC}(\vec{r})] \Psi_i(\vec{r}) = \varepsilon_i \Psi_i(\vec{r}) \text{ with } \rho(\vec{r}) = \sum |\psi_i(\vec{r})|^2} \quad (\text{II-11})$$

By using (II-11) and forming the quantity

$$E_{BS} = \sum_i \varepsilon_i \int \Psi_i^*(r) \Psi_i(r) d^3r = \sum_i \varepsilon_i \quad (\text{II-12})$$

one can compare with total energy expression (II-4) to obtain

$$E_{TOT} = \sum_{i,occ} \varepsilon_i + \int d^3r \rho(\vec{r}) \{ \varepsilon_H - \mu_H + \varepsilon_{XC} - \mu_{XC} \} \quad (\text{II-13})$$

(after convergence of self consistency $\mu_H = 2\varepsilon_H$).

VARIATIONALLY CORRECT ITERATIONS

Although convergence is usually fast and cheap for atomic total energies, it is interesting to explicate the variationally correct iteration scheme which is used by my programs. Errors in E_{TOT} are second order in the density errors $\delta\rho^{(j)} = \rho^j(r) - \rho^{EXACT}(r)$ when the equations are properly formulated. (See ref. 5 for some discussion of errors in E_{TOT}). Thus as $\rho^j(r)$ for iteration j converges toward the exact $\rho(r)$, E_{TOT} converges much faster.

ITERATION SCHEME

$$V^{(0)} = \text{given} \Rightarrow \Psi_i^{(0)}, \varepsilon_i^{(0)} \Rightarrow \rho^{(0)} \Rightarrow \varepsilon_H^{(0)}, \varepsilon_{xc}^{(0)} \left(\text{also } \mu_H^{(0)}, \mu_{xc}^{(0)} \right)$$

$$\Rightarrow E^{(0)} = \int d^3r \left(v(r) + \varepsilon_H^{(0)} + \varepsilon_{xc}^{(0)} \right) \rho^{(0)} + T_o^{(0)}$$

$$V^{(1)} = v(r) + \mu_H^{(0)}(r) + \mu_{xc}^{(0)}(r)$$

$$\Rightarrow \Psi_i^{(1)}, \varepsilon_i^{(1)} \Rightarrow \rho^{(1)} \Rightarrow \varepsilon_H^{(1)}, \varepsilon_{xc}^{(1)}, (\mu_H^{(1)}, \mu_{xc}^{(1)})$$

$$\Rightarrow E^{(1)} = \int d^3r (v(r) + \varepsilon_H^{(1)} + \varepsilon_{XC}^{(1)}) \rho^{(1)} + T_o^{(1)}$$

$$\text{But } \sum \varepsilon_i^{(1)} = T_o^{(1)} + \int v\rho^{(1)} + \int d^3r \rho^{(1)} \left[\mu_H^{(0)} + \mu_{xc}^{(0)} \right]$$

$$\text{Hence } E^{(1)} = \sum \varepsilon_i^{(1)} + \int d^3r \rho^{(1)} \left\{ \varepsilon_{11}^{(1)} - \mu_H^{(0)} + \varepsilon_{xc}^{(1)} - \mu_{xc}^{(0)} \right\}$$

And the variationally correct general scheme is

$$E_{TOT}^{(j)} = \sum_{i=occ} \varepsilon_i^{(j)} + \int d^3r \rho^{(j)}(r) \left\{ \varepsilon_H^{(j)} - \mu_H^{(j-1)} + \varepsilon_{xc}^{(j)} - \mu_{xc}^{(j-1)} \right\} \quad (\text{II-14})$$

Details of implementation are given later.

REDUCTION OF SE (II) TO A RADIAL EQUATION

If $V(\vec{r})$ were spherically symmetric we would use

$$\Psi_{nlm}(\vec{r}) = Y_{lm}(\theta, \phi) \hat{R}_{nl}(r)$$

Define w_{nlm} = electron occupation of state Ψ_{nlm} (evidently 2,1, or 0). Then

$$\begin{aligned} \rho(\vec{r}) &= \sum_{nlm} w_{nlm} |\Psi_{nlm}(\vec{r})|^2 \\ &= \sum_{nl} (\hat{R}_{nl}(r))^2 \sum_{m=-l}^l w_{nlm} |Y_{lm}|^2 \end{aligned}$$

We now spherically average by assuming uniform occupation among various m 's, $w_{nlm'} = w_{nlm}$. Recall (ha ha) from the addition theorem of spherical harmonics

$$\sum_{m=-l}^l |Y_{lm}|^2 = \frac{2l+1}{4\pi}$$

implying the spherically averaged result

$$\rho(|\vec{r}|) = \frac{1}{4\pi} \sum_{nl} \omega_{nl} |\hat{R}_{nl}(r)|^2 \quad (\text{II-15})$$

If $\rho(r)$ is spherically symmetric then so is $V(r)$. The radial SE is obtained by substituting

$$R_{nl}(r) \equiv r \hat{R}_{nl}(r) \quad (\text{II-16})$$

which leads to equation (I-2),

$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2}\right) R_{nl}(r) = \varepsilon_{nl} R_{nl}(r) \quad (\text{II-17})$$

It is useful to define a “radial” charge density $\rho_s(r)$ to accompany $R(r)$,

$$\rho_s(r) = 4\pi r^2 \rho(r) = \sum_{nl} w_{nl} R_{nl}^2(r) \quad (\text{s denotes spherical}) \quad (\text{II-18})$$

Note $\int_0^\infty R_{nl}^2 dr = 1$ and $\int_0^\infty \rho_s(r) dr = N$.

ANGULAR INTEGRATION OF HARTREE POTENTIAL

From Eq. (II-7), the Hartree potential

$$\mu_H(\vec{r}) = 2\varepsilon_H(\vec{r}) = \int \frac{2\rho(r')}{|r-r'|} d^3r'$$

(also see (II-5)) in Rydberg units. Plug in spherically averaged $\rho(r)$ from (II-15)

$$\mu_H(\vec{r}) = 2 \sum_{nl} w_{nl} \int_0^\infty r'^2 dr (\hat{R}_{nl}(r'))^2 \underbrace{\frac{1}{4\pi} \int (r^2 + r'^2 - 2rr' \cos \theta)^{-1/2} d \cos \theta}_{\text{angular term}} dr$$

The bracketed angular term is fairly easily integrated to give

$$\frac{1}{r_{>}} \equiv \begin{cases} \frac{1}{r'} & r' > r \\ \frac{1}{r} & r' < r \end{cases}$$

$$\Rightarrow \mu_H(r) = 2 \sum_{nl} w_{nl} \left\{ \frac{1}{r} \int_0^r dr' R_{nl}^2(r') + \int_r^\infty \frac{R_{nl}^2(r')}{r'} dr' \right\} \quad (\text{II-19})$$

where $R \equiv r\hat{R}$. Recalling the spherically averaged “radial charge density” ρ_s (Eq. II-18),

$$\boxed{\mu_H(r) = 2 \left\{ \frac{1}{r} \int_0^r \rho_s(r') dr' + \int_r^\infty \frac{\rho_s(r')}{r'} dr' \right\}} \quad (\text{II-20})$$

The final result is easy to obtain numerically on a radial grid.

2.1.2 Exchange and correlation (excorr)

Consider excorr potentials $\mu_{xc}(r)$ and excorr energy densities $\varepsilon_{xc}(r)$ (Eqs. (II-3) and (II-8)).

Aim: To develop some version of $\varepsilon_{xc}(\rho(r))$ which reproduces the computed exchange correlation energy of an electron gas at various densities. The resulting $\varepsilon_{xc}(\rho(r))$ is then simply taken over to the solid or atomic problem. We review several classes of ε_{xc} . For an extensive review see Ref. 11. The following notes were copied in part from notes of C.D. Gelatt.

In place of $\rho(r)$ use electron density parameter r_s where

$$r_s = \left(\frac{3}{4\pi\rho(r)} \right)^{1/3}$$

We consider only non-spin-polarized excorr.

EXCHANGE

The pure exchange energy density ε_x is by definition the HF value for a non-interacting uniform electron gas.

$$\begin{aligned} \varepsilon_x(\rho) &= -3 \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3} \text{Ryd} \\ &= -3 \left(\frac{9}{32\pi^2} \right)^{1/3} \frac{1}{r_s} \end{aligned} \quad (\text{II-21})$$

To obtain $\mu_x(r_s)$ note that

$$\frac{\partial}{\partial \rho} = \frac{-1}{3} r_s \frac{4\pi}{3} r_s^3 \frac{\partial}{\partial r_s} \quad (\text{II-22})$$

Thus the pure exchange potential is always (Eq. II-8)

$$\begin{aligned} \mu_x(r_s) &= \varepsilon_x(r_s) + \left(\frac{4\pi}{3} r_s^3 \right)^{-1} \left(\frac{-r_s}{3} \frac{4\pi}{3} r_s^3 \right) \frac{\partial \varepsilon_x}{\partial r_s} \\ &= \varepsilon_x - \left(\frac{r_s}{3} \right) (-\varepsilon_x \cdot r_s^{-1}) \end{aligned}$$

$$\begin{aligned}
\Rightarrow \mu_x(r_s) &= \frac{4}{3}\varepsilon_x(r_s) \\
&= -4 \left(\frac{9}{32\pi^2} \right)^{1/3} \frac{1}{r_s}
\end{aligned} \tag{II-23}$$

CORRELATION

(1) Simplest early attempt is Slater “ $X\alpha$ ” which uses

$$\begin{aligned}
\mu_{xc} &= -6\alpha \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3} \\
&= -6\alpha \left(\frac{9}{32\pi^2} \right)^{1/3} r_s^{-1}
\end{aligned} \tag{II-24}$$

and

$$\varepsilon_{xc} = \frac{3}{4}\mu_{xc}$$

Restrict $\frac{2}{3} \leq \alpha \leq 1$. $\alpha = \frac{2}{3}$ is pure exchange, $\alpha > \frac{2}{3}$ supposedly adds some correlation.

(2) Another simple popular form is Wigner interpolation. This is one of the simplest attempts to fit accurate correlated electron gas results.

In the high density regime ($r_s = 1$) Wigner obtained the numerical result

$$\varepsilon_c(r_s = 1) \simeq -\frac{0.88}{7.8}\text{Ryd}$$

At low density ($r_s \rightarrow \infty$) the electrons condense into a Wigner electron solid. He obtained

$$E_{solid} = -\frac{3}{r_s} + \frac{3}{r_s^{3/2}}$$

The HF energies are $E_{kin} = \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2}$,

$$\begin{aligned}
E_x &= -\frac{3}{2\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s}, \text{ and} \\
E_{pot} &= \frac{6}{5} \frac{1}{r_s} \text{ Ryd} \\
\Rightarrow E_{HF} &= -2.11633 \frac{1}{r_s} + O\left(\frac{1}{r_s^2}\right)
\end{aligned}$$

At low density therefore (to order $r_s^{-3/2}$)

$$\begin{aligned}
E_{corr} &= E_{solid} - E_{HF} \simeq -\frac{0.8837}{r_s} \\
\Rightarrow \varepsilon_c(r_s) &\equiv \left\{ \begin{array}{ll} -\frac{0.88}{7.8} & r_s \text{ small} \\ -\frac{0.88}{r_s} & r_s \text{ large} \end{array} \right\} \\
\varepsilon_c(r_s) &\simeq -\frac{0.88}{r_s + 7.8}
\end{aligned}$$

Thus (Wigner)

$$\begin{aligned}
\varepsilon_c(r_s) &= -\frac{0.88}{r_s + 7.8} \\
\mu_c &= \left(\frac{\frac{4}{3}r_s + 7.8}{r_s + 7.8}\right) \cdot \varepsilon_c \tag{II-25}
\end{aligned}$$

The pure exchange is the usual ε_x, μ_x given in (II-21) and (II-23).

(3) A class of formulas results from an interpolation scheme developed by Hedin and Lundqvist (J. Phys. C. 4, 2064(1971)). By considering numerical electron gas calculations they noticed that

$$\frac{d\mu_{xc}(r_s)}{dr_s} = \gamma(r_s) \frac{d\mu_x(r_s)}{dr_s}$$

gives a function $\gamma(r_s)$ which is nearly a straight line. $\gamma(r_s)$ is fit well by

$$\gamma(r_s) = 1 + \frac{Bx}{1+x}, x = \frac{r_s}{A}$$

Integrating,

$$\mu_{xc}(r_s) = \mu_x(r_s) - C \ln \left(1 + \frac{1}{x} \right) \quad (\text{II-26})$$

with $C = \frac{B}{A}\lambda$, $\mu_{XC}(r_s) = -\frac{\lambda}{r_s}$ (Eq. 23), and

$$\lambda \equiv \left(\frac{18}{\pi^2} \right)^{1/3} = 1.221774 \text{ Ryd.} \quad (\text{II-27})$$

Integrating again,

$$\varepsilon_{xc}(r_s) = \varepsilon_x(r_s) - C \left\{ (1 + x^3) \ln \left(1 + \frac{1}{x} \right) + \frac{x}{2} - x^2 - \frac{1}{3} \right\} \quad (\text{II-28})$$

with $\varepsilon_x = \frac{3}{4}\mu_x = -\frac{3}{4}\frac{\lambda}{r_s}$

Others fit the numerical calculation with $A=21$ a.u. (Bohr), $C = 0.045$ Ryd.

The asymptotic limits of $\varepsilon_c \leq \varepsilon_{xc} - \varepsilon_x$ are $\varepsilon_c(r_s \rightarrow 0) \rightarrow +C \ln r_s$ and

$$\varepsilon_c(r_s \rightarrow \infty) = -C \left\{ \frac{3A}{4r_s} - \frac{3}{10} \left(\frac{A}{r_s} \right)^2 + \frac{3}{18} \left(\frac{A}{r_s} \right)^3 - \frac{3}{28} \left(\frac{A}{r_s} \right)^4 + \frac{3}{40} \left(\frac{A}{r_s} \right)^5 - \dots + (-1)^{n-1} \frac{3}{n(n+3)} \left(\frac{A}{r_s} \right)^n + \dots \right\} \quad (\text{II-29})$$

(actually used to facilitate numerical evaluation)

$$\cong -\frac{3CA}{4r_s}$$

Ulf von Barth: To obtain agreement with exact electron gas results in limits $r_s \rightarrow 0$ and $r_s \rightarrow \infty$ modify equation for $\gamma(r_s)$ by including a second set of A's and B's

$$\Rightarrow \mu_c(r_s) = - \sum_{i=1}^2 C_i \ln \left(1 + \frac{1}{x_i} \right); x_i = \frac{r_s}{A_i}$$

$$\varepsilon_c(r_s) = - \sum_{i=1}^2 C_i \left\{ (1 + x_i) \ln \left(1 + \frac{1}{x_i} \right) + \frac{x_i}{2} - x_i^2 - \frac{1}{3} \right\} \quad (\text{II-30})$$

$$\begin{aligned} \varepsilon_c(r_s \rightarrow 0) &\rightarrow + (C_1 + C_2) \ln r_s \\ \varepsilon_c(r_s \rightarrow \infty) &\rightarrow - \frac{3 C_1 A_1 + C_2 A_2}{4 r_s} \end{aligned}$$

To choose parameters compare with

(a) RPA result for $r_s \rightarrow 0$

$$\varepsilon_c = \underbrace{\left(\frac{2}{\pi^2} \right) (1 - \ln(2))}_{0.06218} \ln(r_s) - .096 + \mathcal{O}(r_s \ln(r_s)) \text{ Ryd}$$

(see p. 166 of Fetter and Walecke)

(b) binding energy of BCC electron lattice is

$$E = -1.791862/r_s \text{ Ryd}$$

von Barth chose parameters

$$\begin{aligned} A_1 &= 32.5 \text{ au}, & A_2 &= 0.8 \text{ au} \\ C_1 &= 0.0352 \text{ Ryd}, & C_2 &= 0.0270 \text{ Ryd} \end{aligned} \quad , \quad \text{giving}$$

$$\begin{aligned} \varepsilon_c(r_s \rightarrow 0) &\rightarrow 0.0622 \ln(r_s) \\ \varepsilon_{XC}(r_s \rightarrow \infty) &\rightarrow - \frac{3}{4 r_s} (\lambda + C_1 A_1 + C_2 A_2) = -1.790531/r_s \end{aligned}$$

Gelatt has computed Cu ($d^{10}s$) non-spin-polarized total energies using HL and vB schemes:

$$\begin{aligned} E_{TOT}^{HL} &= -3275.4391 \text{ Ryd} \\ E_{TOT}^{vB} &= -3275.6392 \text{ Ryd} \end{aligned}$$

A brief note on spin polarized local exchange and correlation (see Ref. 11 for discussion):

$$\begin{aligned}
\text{Define polarization } \xi &= \frac{\rho^\uparrow - \rho^\downarrow}{\rho^\uparrow + \rho^\downarrow} \\
\text{and } g(\xi) &= \frac{(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2}{2^{4/3} - 2} \\
\text{then } \varepsilon_{XC}(r_s, \xi) &= \varepsilon_{XC}(r_s, 0) + g(\xi)[\varepsilon_{XC}(r_s, 1) - \varepsilon_{XC}(r_s, 0)] \\
\text{where } \varepsilon_{XC}(r_s, 0) &= \varepsilon_X(r_s) - C_0 f(r_s/r_0) \\
\varepsilon_{XC}(r_s, 1) &= 2^{4/3} \varepsilon_X(r_s) - C_1 f(r_s/r_1) \\
\text{and } f(y) &\equiv (1 + y^3) \ln(1 + 1/y) + y/2 - y^2 - 1/3.
\end{aligned}$$

This is the Hedin-Lundqvist type of expression seen before.

A sampling of spin-polarized parameterizations.

	a	b	c	d
r_0	39.7	11.4	30	21
C_0	0.0461	0.0666	0.0504	0.045
r_1	70.6	15.9	75	52.9
C_1	0.0263	0.0406	0.0254	0.0225

a) Rajagopal, 1977 (Ref 11).

b) O. Gunnarson and BI Lundqvist PRB 13, 4274 (1976).

c) Hedin and Lundqvist ? See Ref 11.

d) See Ref 11.

Perdew-Zunger Parameterization of Ceperly-Alder Electron Gas (PZCA)⁴
See Ref 6. (UNPOLARIZED)

$$\begin{aligned}
\varepsilon_C &= \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} & \text{(II-31)} \\
r_s \geq 1, \quad \mu_C &= \left(1 - \frac{r_s}{3} \frac{d}{dr_s}\right) \varepsilon_C
\end{aligned}$$

⁴BHS, Ref 2. They misprint the value of γ .

$$\Rightarrow \mu_C = \varepsilon_C \left(\frac{1 + \frac{7}{6}\beta_1\sqrt{r_s} + \frac{4}{3}\beta_2 r_s}{1 + \beta_1\sqrt{r_s} + \beta_2 r_s} \right) \quad (\text{II-32})$$

At high density ($r_s < 1$) leading terms are

$$\varepsilon_C(r_s) = A \ln(r_s) + B + Cr_s \ln(r_s) + Dr_s \quad (\text{II-33})$$

$$\mu_C(r_s) = A \ln(r_s) + \left(B - \frac{1}{3}A\right) + \frac{2}{3}Cr_s \ln(r_s) + \frac{1}{3}(2D - C)r_s. \quad (\text{II-34})$$

From RPA result,

$$\begin{aligned} A &= \frac{2}{\pi^2}(1 - \ln(2)) \quad \text{Ryd} \\ B &= -0.096 \quad \text{Ryd.} \end{aligned}$$

For Perdew-Zunger:

$$\begin{aligned} \gamma &= -0.1423 \text{ Hartrees} = -0.2846 \text{ Ryd} \\ \beta_1 &= 1.0529, \beta_2 = 0.3334 \\ C &= 0.0040 \text{ Ryd}, D = -0.0232 \text{ Ryd} \end{aligned}$$

Finally PZCA excorr is

$$\varepsilon_{XC}(r_s) = \varepsilon_X(r_s) + \begin{cases} \frac{-a_1}{1+a_2\sqrt{r_s}+a_3r_s} & ; r_s \geq 1 \\ -b_1 + (b_2 + b_3 r_s) \ln(r_s) - b_4 r_s & ; r_s < 1 \end{cases} \quad (\text{II-35})$$

$$\text{Continuity} \Rightarrow \frac{a_1}{1+a_2+a_3} = b_1 + b_4.$$

$$\text{Check: } \frac{0.2846}{1+1.0529+0.3334} = 0.11926 ; b_1 + b_4 = 0.096 + 0.0232 = 0.1192.$$

$$\frac{d\varepsilon_C}{dr_s} = \begin{cases} \frac{a_1}{(1+a_2\sqrt{r_s}+a_3r_s)^2} \left(\frac{a_2}{2\sqrt{r_s}} + a_3 \right) & ; r_s \geq 1 \\ -b_4 + \left(\frac{b_2}{r_s} + b_3 \right) + b_3 \ln(r_s) & ; r_s < 1 \end{cases} \quad (\text{II-36})$$

$$\text{Continuity} \Rightarrow \frac{a_1}{(1+a_2+a_3)^2} \left(\frac{a_2}{2} + a_3 \right) = b_2 + b_3 - b_4$$

$$\text{Check: } LHS = 0.042974 \quad RHS = 0.04298$$

PZCA (Parameters in Ryd):

$$\begin{aligned} a_1 &= 0.2846 & b_1 &= 0.096 \\ a_2 &= 1.0529 & b_2 &= \frac{2}{\pi^2}(1 - \ln(2)) = 0.06218 \\ a_3 &= 0.3334 & b_3 &= 0.0040 \\ & & b_4 &= 0.0232 \end{aligned}$$

PZ have a similarly parameterized spin-polarized version. See ref. 6.

SUMMARY

We have mentioned several schemes for putting in correlation beyond the local exchange energy density $\varepsilon_X(r_s) = -\frac{3}{4} \frac{\lambda}{r_s}$.

1. Slater $X\alpha$ with $\alpha > 2/3$ for correlation
2. Wigner interpolation formula
3. The Hedin-Lundqvist class of formulas
4. Extension of HL by von Barth
5. Perdew-Zunger

This last is the most accurate, although it is not obvious that an accurate fit to the electron gas is worth it.

2.2 Pseudopotentials (all soft core)

2.2.1 Non-norm conserving

Choose a reference configuration (e.g. the ground state) for the atom and solve the self-consistent all-electron problem for $V(r)$, $R_{nl}(r)$, and ε_{nl} . Let R_l represent a given valence state of angular momentum l .

$$R_l'' = \left(V(r) + \frac{l(l+1)}{r^2} - \varepsilon_l \right) R_l \quad (\text{II B-1})$$

$$f(r/r_c) \equiv e^{-(r/r_c)^\lambda}, \lambda \approx 3.5 \quad (\text{see ref 2}) \quad (\text{II B-2})$$

$$V_{1,l}(r) \equiv (1 - f(r/r_c))V(r) + C_l f(r/r_c) \quad (\text{II B-3})$$

$$\omega_{1,l}'' = \left(V_{1,l}(r) + \frac{l(l+1)}{r^2} - \tilde{\varepsilon}_l \right) \omega_{1,l}. \quad (\text{II B-4})$$

Adjust C_l to make $\tilde{\varepsilon}_l = \varepsilon_l$.

{How this is done: First guess a C_l . Then use PT

$$\begin{aligned} \Rightarrow \delta\varepsilon &\approx \langle \omega_1 | \delta V | \omega_1 \rangle = \langle \omega_1 | f(r/r_c) \delta C | \omega_1 \rangle \\ &= (\delta C) \langle \omega_1 | f(r/r_c) | \omega_1 \rangle \equiv \delta C Q. \end{aligned}$$

$Q = \int_0^\infty \omega_1^2(r) f(r/r_c) dr$ is easily computed for a given $C^{(i)}$. Thus one adjusts $C^{(i)}$ by $\delta C^{(i)}$ given by $\delta C^{(i)} = (\varepsilon_l - \tilde{\varepsilon}_l^{(i)})/Q^{(i)}$ until the difference gets small enough. It usually converges in 6 or fewer iterations }.

From (II-9) note that $V_{1,1}(r) \rightarrow V(r)$ for $r \gg r_c$. Thus it must hold that $\gamma\omega_1(r) = R(r)$ for $r \gg r_c$. Usually $\gamma \approx 1$ but $\gamma \neq 1$ (we assume both ω_1 and R are normalized).

$V_{1,l}(r)$ is the nonlocal non-norm-conserving psp.

2.2.2 Norm-conserving

(Refs. 1,2,9)

Idea: make the wavefunction identical to AE result $R(r)$ for $r \gg r_c$. Thus define a $\omega_2(r) = \gamma\omega_1(r) = R(r)$ for $r \gg r_c$. To keep $\int_0^\infty \omega_2^2(r) dr = 1$, need to change core region. Define γ such that

$$\gamma\omega_1(2r_m) = R(2r_m), \quad (\text{II B-5})$$

where $r_m =$ radius of last maximum in $R(r)$.

$$\omega_2(r) \equiv \gamma(\omega_1(r) + \delta r^{l+1} f(r/r_c)). \quad (\text{II B-6})$$

The r^{l+1} gives $\omega_2(r)$ the core behavior as $r \rightarrow 0$. Evidently $\omega_2(r \gg r_c) = R(r)$ as desired. Now adjust δ to solve

$$\int_0^\infty \omega_2^2(r) dr = 1 \quad (\text{II B-7})$$

$\omega_2(r)$ is the norm conserving wavefunction for the following reason:

$$\int_0^r \omega_2^2(r') dr' = \int_0^r R^2(r') dr' \quad \text{for } r \gg r_c. \quad (\text{II B-8})$$

One consequence is that the amount of charge in the core region is the same for real and ps wavefunctions. The most ingenious part of the improvement relates to the logarithmic derivatives of the real and pseudo wavefunctions. Since the wavefunction $R(r)$ is exactly reproduced outside the core, so is the logarithmic derivative

$$\beta(r, \varepsilon) \equiv \frac{d \ln(R(r, \varepsilon))}{dr} = \frac{1}{R} \frac{dR}{dr} \quad (\text{II B-9})$$

at the particular eigenenergy ε . $\beta(r, \varepsilon)$ over a range of energies actually describes the scattering properties of the potential.

For V^{PS} to mimic V^{AE} and to be transferable to other systems, β^{PS} must track β^{AE} over same range of energies of interest (see Refs. 1,2, [4](#)). We will now show that the slope $\frac{d\beta}{d\varepsilon}$ is also matched exactly as long as Eq. (II B-8) is satisfied.

$$\begin{aligned} (1) \Rightarrow \frac{R''}{R} &= \frac{l(l+1)}{r^2} + V(r) - \varepsilon = \frac{d^2 \ln(R)}{dr^2} + \left(\frac{d \ln(R)}{dr} \right)^2 \\ \Rightarrow \frac{d}{d\varepsilon} \left\{ \frac{d^2 \ln(R)}{dr^2} + \left(\frac{d \ln(R)}{dr} \right)^2 \right\} &= \frac{1}{R^2} \frac{d}{dr} \left(R^2 \frac{d}{d\varepsilon} \frac{d \ln(R)}{dr} \right) = -1 \\ \Rightarrow R^2 \frac{d}{d\varepsilon} \left(\frac{d \ln(R)}{dr} \right) \Big|_{r, \varepsilon} &= - \int_0^r R^2(r', \varepsilon) dr' \end{aligned} \quad (\text{II B-10})$$

Therefore, $\frac{d}{d\varepsilon} \frac{d \ln(\omega_2)}{dr} \Big|_{r, \varepsilon} = \frac{d}{d\varepsilon} \left(\frac{d \ln(R)}{dr} \right) \Big|_{r, \varepsilon}$ for $r \gg r_c$.

Solving (II B-7) for δ :

$$\begin{aligned} \gamma^2 \{1 + 2\delta a_2 + \delta^2 a_4\} &= 1, \quad \text{where} \\ a_2 &= \int_0^\infty \omega_1(r) r^{l+1} f(r/r_c) dr \\ a_4 &= \int_0^\infty r^{2l+2} e^{-2(r/r_c)^\lambda} dr \end{aligned}$$

Evaluate a_2 numerically for a given $\omega_1(r)$.

$$a_4 = \left(\frac{r_c}{2^{1/\lambda}} \right)^{2l+3} \frac{1}{\lambda} \Gamma \left(\frac{2l+3}{\lambda} \right) \quad (\text{II B-11})$$

(since $\int_0^\infty x^{\nu-1} e^{-\mu x^p} dx = \frac{1}{|p|} \mu^{-\nu/p} \Gamma(\nu/p)$.)

$$\Rightarrow \delta = -\frac{a_2}{a_4} + \left[\left(\frac{a_2}{a_4} \right)^2 - \frac{1 - 1/\gamma^2}{a_4} \right]^{1/2} \quad (\text{II B-12})$$

for smaller root δ (I assume $a_2 > 0$). As expected, $\gamma = 1 \Rightarrow \delta = 0$.

After δ is obtained, one has $\omega_2(r)$ from Eq. (II B-6). The norm conserving psp $V_2(r)$, of which $\omega_2(r)$ is an eigenfunction, is obtained from the SE.

$$\begin{aligned} V_2(r) &= \frac{\omega_2''}{\omega_2} + \varepsilon - \frac{l(l+1)}{r^2} = V_1 + \left(\frac{\omega_2''}{\omega_2} - \frac{\omega_1''}{\omega_1} \right) \\ \omega_2'' &= \gamma \omega_1'' + \gamma \delta (r^{l+1} f(r))'' \\ \gamma \omega_1'' &= \left(V_1 + \frac{l(l+1)}{r^2} - \varepsilon \right) (\omega_2 - \gamma \delta r^{l+1} f(r)) \end{aligned}$$

$$\begin{aligned}
\frac{d^2}{dr^2} \left(r^{l+1} e^{-(r/r_c)^\lambda} \right) &= \left\{ \frac{l(l+1)}{r^2} + \left(\frac{r}{r_c} \right)^{2\lambda-2} \frac{\lambda^2}{r_c^2} \right. \\
&\quad \left. - \left(\frac{r}{r_c} \right)^{\lambda-2} \left[\frac{\lambda(\lambda-1)}{r_c^2} + \frac{2(l+1)\lambda}{r_c^2} \right] \right\} r^{l+1} e^{-(r/r_c)^\lambda} \\
\Rightarrow \left(\frac{\omega_2''}{\omega_2} - \frac{\omega_1''}{\omega_1} \right) &= \frac{\gamma\delta}{\omega_2} \left\{ r^{l+1} e^{-(r/r_c)^\lambda} \left[\frac{l(l+1)}{r^2} \right. \right. \\
&\quad \left. \left. + \frac{1}{r^2} \left\{ \lambda^2 \left(\frac{r}{r_c} \right)^{2\lambda} - \left(\lambda(\lambda-1) + 2\lambda(l+1) \left(\frac{r}{r_c} \right)^\lambda \right) \right\} \right] \right\} \\
&\quad - r^{l+1} e^{-(r/r_c)^\lambda} \left[V_1(r) + \frac{l(l+1)}{r^2} - \varepsilon \right] \\
&= \gamma\delta \left(\frac{r^{l+1}}{\omega_2(r)} \right) e^{-(r/r_c)^\lambda} \left\{ \frac{1}{r^2} \left[\lambda^2 \left(\frac{r}{r_c} \right)^{2\lambda} \right. \right. \\
&\quad \left. \left. - (\lambda(\lambda-1) + 2\lambda(l+1)) \left(\frac{r}{r_c} \right)^\lambda \right] + \varepsilon - V_1(r) \right\}
\end{aligned}$$

Notice that this ‘‘norm conserving correction’’ term only changes V^{PS} in the core region, because of the factor $e^{-(r/r_c)^\lambda}$. Investigate correction as $r \rightarrow 0$. We know $\omega_1(r) \propto r^{l+1}$ as $r \rightarrow 0$; say $\omega_1(r) \approx Q_1 r^{l+1}$. Then $\omega_2(r) \approx \gamma(Q_1 + \delta) r^{l+1}$. The terms with $r^{2\lambda}/r^2$ and r^λ/r^2 are at least $\mathcal{O}(r)$, while $V_1(r \rightarrow 0) = C$ Eq. (II B-3). Thus

$$\left(\frac{\omega_2''}{\omega_2} - \frac{\omega_1''}{\omega_1} \right) \approx \frac{\gamma\delta}{\gamma(Q_1 + \delta)} (\varepsilon - C) \quad \text{as } r \rightarrow 0.$$

This is evidently not singular unless $Q_1 + \delta \approx 0$.

Finally the screened norm conserving psp is given by

$$\begin{aligned}
V_2(r) &= V_1(r) + \gamma\delta \left(\frac{r^{l+1}}{\omega_2} \right) e^{-(r/r_c)^\lambda} \left\{ \frac{1}{r^2} \left[\lambda^2 \left(\frac{r}{r_c} \right)^{2\lambda} \right. \right. \\
&\quad \left. \left. - (\lambda(\lambda-1) + 2\lambda(l+1)) \left(\frac{r}{r_c} \right)^\lambda \right] + \varepsilon - V_1(r) \right\}
\end{aligned} \tag{II B-13}$$

For each angular momentum l a separate calculation gives a $V_{2,l}(r)$. The resulting pseudowavefunctions $\omega_{2,l}(r)$ are used to generate a (valence) charge

density, which is then used to obtain the Hartree and excorr screening potentials. These are then subtracted from each $V_{2,l}(r)$ to obtain ionic or core psp.

2.2.3 Extended norm conserving

(see Ref. 9)

We have carried the matching of logarithmic derivatives $\beta(r, \varepsilon) = \frac{\partial}{\partial r}(\ln R(r, \varepsilon))$ one step further by discovering an identity which lets us match second energy derivatives:

$$\left. \frac{\partial^2}{\partial \varepsilon^2} \beta^{PS}(r, \varepsilon) \right|_{r, \varepsilon_l} = \left. \frac{\partial^2}{\partial \varepsilon^2} \beta^{AE}(r, \varepsilon) \right|_{r, \varepsilon_l}$$

for $r > r_c$ and $\varepsilon_l = \text{eigenenergy}$.

Differentiate again the line above Eq. (II B-10) to get

$$\begin{aligned} & \frac{\partial^2}{\partial \varepsilon^2} \left[\frac{d^2 \ln R}{dr^2} + \left(\frac{d \ln R}{dr} \right)^2 \right] = 0 \\ \Rightarrow & \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial^2 \ln R}{\partial r^2} + 2 \left(\frac{\partial}{\partial \varepsilon} \frac{\partial \ln R}{\partial r} \right)^2 + 2 \frac{\partial \ln R}{\partial r} \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln R}{\partial r} = 0 \\ \Rightarrow & \frac{1}{R^2} \frac{\partial}{\partial r} \left(R^2 \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln R}{\partial r} \right) = -2 \left(\frac{\partial}{\partial \varepsilon} \frac{\partial \ln R}{\partial r} \right)^2 \\ \text{or} & \frac{\partial}{\partial r} \left(R^2 \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln R}{\partial r} \right) = -2R^2 \left(\frac{\partial}{\partial \varepsilon} \frac{\partial \ln R}{\partial r} \right)^2 \end{aligned} \quad (\text{II B-14})$$

As long as $R(r) \neq 0$ (for a pseudowavefunction $\omega_2(r)$) Eq. (II B-10) \Rightarrow

$$\frac{\partial}{\partial \varepsilon} \left(\frac{\partial \ln R}{\partial r} \right) = -\frac{1}{R^2(r)} \int_0^r R^2(r') dr'$$

Combining with Eq. (II B-14),

$$R^2 \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln R}{\partial r} \Big|_{r, \varepsilon} = -2 \int_0^r \left\{ \frac{-\int_0^{r'} R^2(r'') dr''}{R(r')} \right\}^2 dr' \quad (\text{II B-15})$$

as long as $R(r') \neq 0$.

Eq. (II B-15) is the analog of Eq. (II B-10).

If $R(r)$ has nodes then division by $R^2(r)$ is disallowed. Thus for the real all-electron $R(r)$, evaluate the LHS of Eq. (II B-15) directly from

$$-2Q'(r) \equiv R^2(r, \varepsilon) \frac{\partial}{\partial \varepsilon'} \left\{ \frac{-\int_0^r R^2(r', \varepsilon') dr'}{R^2(r, \varepsilon')} \right\} \Big|_{\varepsilon'=\varepsilon} \quad (\text{II B-16})$$

where $R^2(r, \varepsilon') = \frac{\partial}{\partial \varepsilon} \left(\frac{\partial \ln R}{\partial r} \right) \Big|_{\varepsilon'}$

for $r >$ any nodes; that is usually $r \gg r_c$.

An extended norm conserving wavefunction $\omega_3(r)$ will be required to satisfy

$$\int_0^r \left(\frac{\int_0^{r'} \omega_3^2(r'') dr''}{\omega_3(r')} \right)^2 dr' = Q'(r) \quad (\text{II B-17})$$

for $r > r_c$.

$\omega_3(r)$ must also satisfy norm conservation, Eq. (II B-18). For such a wavefunction, Eq. (II B-15) shows that

$$\frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln \omega_3}{\partial r} \Big|_{r, \varepsilon} = \frac{\partial^2}{\partial \varepsilon^2} \frac{\partial \ln R}{\partial r} \Big|_{r, l}$$

for $r > r_c$ and ε =eigenvalue.

IMPLEMENTATION

$Q'(r)$ is obtained numerically (take energy derivative by differences) for some particular $r > r_c$ using Eq. (30). $\omega_1(r)$ is found as in the methods described above. Then, using a HSC type of scheme,

$$\omega_3(r) = \gamma \left[\omega_1(r) + \underbrace{(\delta r^2 + \eta r^3)}_{\text{chosen to keep } v_3(r \rightarrow 0) \text{ finite}} r^{l+1} e^{-\left(\frac{r}{r_c}\right)^\lambda} \right] \quad (\text{II B-18})$$

As before, γ is fit to make $\omega_3(r) = R(r)$ for $r \gg r_c$. δ and η are fit to satisfy overall normalization and Eq. (II B-17). Solving Eq. (II B-17)

gets a bit messy because of the indefinite integral of $\omega_3(r)$. The following six functions are needed on the radial grid:

$$\begin{aligned}
a_1(r) &= \int_0^r \omega_1^2(r') dr' \\
a_2(r) &= \int_0^r \omega_1 r'^{(l+3)} f(r') dr' \\
a_3(r) &= \int_0^r \omega_1 r'^{(l+4)} f(r') dr' \\
a_4(r) &= \int_0^r r'^{(2l+6)} f^2(r') dr' \\
a_5(r) &= \int_0^r r'^{(2l+7)} f^2(r') dr' \\
a_6(r) &= \int_0^r r'^{(2l+8)} f^2(r') dr'
\end{aligned}$$

where $f(r) = e^{-\left(\frac{r}{r_c}\right)^\lambda}$.

Then for a given value of η , normalization requires δ such that

$$\gamma^2[1 + 2\delta a_2 + 2\eta a_3 + \delta^2 a_4 + 2\delta\eta a_5 + \eta^2 a_6] = 1$$

where each a_i is evaluated at some $r \gg r_c$ (effectively $r \rightarrow \infty$).

As a function of η ,

$$\delta(\eta) = -\frac{a_2 + \eta a_5}{a_4} + \left[\left(\frac{a_2 + \eta a_5}{a_4} \right)^2 - \frac{\eta^2 a_6 + 2\eta a_3 + \left(1 - \frac{1}{\gamma^2}\right)}{a_4} \right]^{\frac{1}{2}}$$

To implement Eq. (II B-17), define

$$W(r) = \int_0^r \omega_3^2(r') dr' = \gamma^2[a_1(r) + 2\delta a_2(r) + 2\eta a_3(r) + \delta^2 a_4(r) + 2\delta\eta a_5(r) + \eta^2 a_6(r)]$$

where $\delta = \delta(\eta)$ as above.

Use Eq. (II B-18) to define $\omega_3(r)$ as a function of η and $\delta(\eta)$ and secant or other methods to solve for η such that

$$\int_0^r \left(\frac{W(r')}{\omega_3(r')} \right)^2 dr' = Q(r')$$

for some $r > r_c$.

Having δ and η , the extended norm conserving wavefunction is known and the accompanying psp is obtained as before, from the SE. For reference (not because it is interesting) I include the algebra for the solution for $V_3(r)$.

$$\begin{aligned} \text{Let } g(r) &\equiv r^{l+1} e^{-\left(\frac{r}{r_c}\right)^2} \\ \text{and } h(r) &\equiv (\delta + \eta r)r^2 \end{aligned}$$

$$\Rightarrow \omega_3(r) = \gamma(\omega_1 + h(r)g(r))$$

$$\begin{aligned} \omega_3'' &= \gamma(\omega_1'' + h''g + 2h'g' + hg'') \\ &= (V_1 + \frac{l(l+1)}{r^2} - \varepsilon)(\omega_3 - \gamma hg) + \gamma(h''g + 2h'g' + hg'') \end{aligned}$$

$$g' = \left[(l+1) - \lambda \left(\frac{r}{r_c}\right)^\lambda \right] \frac{1}{r} g(r)$$

$$g'' = \left[\frac{l(l+1)}{r} + (\lambda^2 \left(\frac{r}{r_c}\right)^{2\lambda}) - (\lambda(\lambda-1) + 2\lambda(l+1)) \left(\frac{r}{r_c}\right)^\lambda \frac{1}{r^2} \right] g(r)$$

$$\left(\frac{\omega_3''}{\omega_3} - \frac{\omega_1''}{\omega_1} \right) = \frac{\gamma g(r)}{\omega_3(r)} \left[h'' + \frac{2h'}{r} (l+1 - \lambda y) + \frac{h}{r^2} ((\lambda y)^2 - (\lambda(\lambda-1) + 2\lambda(l+1))y) + h(\varepsilon - V_1(r)) \right]$$

where $y \equiv \left(\frac{r}{r_c}\right)^\lambda$.

To keep V_3 ($r \rightarrow 0$) finite (soft core), must require $r^\lambda \frac{h(r)}{r^2}$, $\frac{h'(r)}{r^2}$, and $h''(r)$ not ∞ as $r \rightarrow 0$.

For $\lambda > 2 \Rightarrow h(r)$ may have a constant term (as in $h(r) = \delta$ for HSC norm-conserving psp). $\frac{h'}{r}$ disallows a linear term.

Our choice above was $h(r) = \delta r^2 + \eta r^3$, which satisfies those restrictions. $h(r) = \delta + \eta r^2$ also works, but not always.

As mentioned earlier, sometimes $Q_1 + \delta \rightarrow 0$ for better choice, leaving $V_3(r)$ singular or awfully large at $r = 0$.

Plug in $h' = (2\delta + 3\eta r)r$ and $h'' = 2\delta + 6\eta r$ and use

$$V_3(r) = \left(\frac{\omega_3''}{\omega_3} - \frac{\omega_1''}{\omega_1} \right) + V_1(r)$$

to finally obtain extended norm cons psp.

$V_3(r)$ is usually small near $r = 0$, like $V_2(r)$ but can tend to have sharper variations than $V_2(r)$ and be less easily used in a plane wave crystal calculation. See Ref. 9.

SUMMARY

We have presented three nonlocal psp based on cutting off the $-\frac{2Z}{r}$ part of $V(r)$ in the core region and replacing it with a constant c or nearly a constant. These were:

1. Non-norm conserving V_1 . Remains const c in core, but pseudowavefunction $\omega_1(r) \neq R(r)$ outside r_c .
2. Norm conserving $V_2(r)$. Cluge up core to make $\omega_2(r) = R(r)$ for $r \gg r_c$.
3. Extended $V_3(r)$. Cluge some more to satisfy some conditions on where the core charge is located.

Each version successively improves the logarithmic derivatives over energies near the eigenvalue. This presumably improves the transferability of the resulting psp.

2.3 Frozen core calculations

I identify what terms contribute to a frozen core calculation of eigenvalues and total energy. Recall AE result (Eq. II-14)

$$E_{TOT}^j = \sum_{j=occ} \varepsilon_i^j + \int_0^\infty dr \rho_s^j(r) [\varepsilon_H^j - \mu_H^{j-1} + \varepsilon_{XC}^j - \mu_{XC}^{j-1}]$$

where I use $\rho_s(r) = 4\pi r^2 \rho(r)$, so that the angular integrals are already included.

To “freeze the core” means to not allow core state wavefunctions to adjust self-consistently. Thus we select a reference state, carry out the SC AE calc, then save the core charge density

$$\rho_{sc}(r) = \sum_{nl}^{core} \omega_{nl} R_{nl}^2(r) \quad (\text{II C-1})$$

For any other arbitrary configuration (as always, specified by $\{\omega_{nl}\}$ - in this case only valence occupations can change), each iteration produces a valence charge density

$$\rho_{sv}^{(j)}(r) \equiv \sum_{nl}^{valence} \omega_{nl} (R_{nl}^{(j)}(r))^2 \quad (\text{II C-2})$$

so the total charge density for a given iteration j is

$$\rho_s^{(j)}(r) = \rho_{sc}(r) + \rho_{sv}^{(j)}(r) \quad (\text{II C-3})$$

—Aside on nonlinearity of excorr (see Ref. 10). Note that Hartree potential terms $\mu_H^{(j)}$ are linear in $\rho_s(r)$,

$$\mu_H^j(r) = \mu_{Hc}(r) + \mu_{Hv}^j(r)$$

but excorr is not linear,

$$\mu_{xc}^j \neq \mu_{xcc}(r) + \mu_{xcv}(r)$$

where $\mu_{xcc}(r) = \mu_{xc}(f_{sc}(r))$ etc.

Unless ρ_{sc} is somehow saved and used in conjunction with psp’s, the psp approx usually linearizes $\mu_{xc}(r)$. The frozen core approx does not linearize

this term, as will be shown.

Define core and valence eigenvalue sums:

$$E_{Bsc}^j = \sum_{nl}^{core} \varepsilon_{nl} \omega_{nl} \quad E_{Bsv}^j = \sum_{nl}^{valence} \varepsilon_{nl} \omega_{nl} \quad (\text{II C-4})$$

From the discussion leading up to Eq. (II C-4),

$$E_{Bsc}^{(j)} = T_0^{(j)} + \int \rho_{sc}^{(j)} \nu dr + \int \rho_{sc}^{(j)} (\mu_H^{(j-1)} + \mu_{XC}^{(j-1)}) dr$$

Separate out terms which are truly fixed when the core $\rho_{sc}(r)$ is frozen – call that term $E_F \equiv E_{FROZEN}$. (see Ref. 5 for more discussion of these separations.)

$$\begin{aligned} E_{TOT}^{(j)} &= (T_c^{(j)} + \int \rho_{sc}^{(j)} \nu + \int \rho_{sc}^{(j)} (\mu_{Hc}^{(j-1)} + \mu_{Hv}^{(j-1)}) + \int \rho_{sc}^{(j)} \mu_{xc}^{(j-1)}) \\ &+ (T_v^{(j)} + \int \rho_{sv}^{(j)} \nu + \int \rho_{sv}^{(j)} (\mu_{Hc}^{(j-1)} + \mu_{Hv}^{(j-1)}) + \int \rho_{sv}^{(j)} \mu_{xc}^{(j-1)}) \\ &+ \int (\rho_{sc}^{(j)} + \rho_{sv}^{(j)}) (\varepsilon_{Hc}^{(j)} + \varepsilon_{Hv}^{(j)} - \mu_{Hc}^{(j-1)} - \mu_{Hv}^{(j-1)} + \varepsilon_{xc}^{(j)} - \mu_{xc}^{(j-1)}) \end{aligned}$$

from

$$(E_{Bsc}^{(j)}) + (E_{Bsv}^{(j)}) + \int \rho_s (\varepsilon_H - \mu_H + \varepsilon_{xc} - \mu_{xc}).$$

Then

$$\begin{aligned} E_{TOT}^{(j)} &= \left\{ T_c + \int \rho_{sc} \nu + \int \rho_{sc} \varepsilon_{Hc} \right\} \\ &+ \left\{ \int \rho_{sc} \varepsilon_{Hv} + \int \rho_{sv} \varepsilon_{Hc} + \int (\rho_{sc} + \rho_{sv}) \varepsilon_{xc} \right\} \\ &+ \left\{ T_v + \int \rho_{sv} \nu + \int \rho_{sv} \varepsilon_{Hv} \right\} \end{aligned}$$

The only part which remains frozen is

$$E_F \equiv T_c + \int \rho_{sc} \nu + \int \rho_{sc} \varepsilon_{Hc}$$

$$\Rightarrow E_F^{(j)} = E_{Bsc}^{(j)} + \int \varepsilon_{Hc}^{(j)} \rho_{sc}^{(j)} - \int \rho_{sc}^{(j)} (\mu_H^{(j-1)} + \mu_{xc}^{(j-1)}) \quad (\text{II C-5})$$

The remaining adjustable part of E_{TOT} is

$$\tilde{E}^{(j)} \equiv E_{TOT}^{(j)} - E_F = T_v^{(j)} + \int \rho_{sc}^{(j)} \nu + \int \rho_{sv}^{(j)} (2\varepsilon_{Hc}^{(j)} + \varepsilon_{Hv}^{(j)}) + \int \rho_s^{(j)} \varepsilon_{xc}^{(j)}$$

where I have used $\int \rho_{sc} \varepsilon_{Hv} = \int \rho_{sv} \varepsilon_{Hc}$.

$$\text{Since } E_{Bsv} = T_v + \int \rho_{sv} \nu + \int \rho_{sv} (\mu_H + \mu_{xc}),$$

$$\tilde{E}^{(j)} = E_{Bsv}^{(j)} + \int \rho_{sv}^{(j)} (2\varepsilon_{Hc} + \varepsilon_{Hv}^{(j)} - \mu_H^{(j-1)} - \mu_{xc}^{(j-1)}) + \int \rho_s^{(j)} \varepsilon_{xc}^{(j)} \quad (\text{II C-6})$$

($2\varepsilon_{Hc}$ is frozen if FC calculation)

Summary of this part:

$$\begin{aligned} E_{TOT} &= E_{Bs} + \int \rho_s (\varepsilon_H - \mu_H + \varepsilon_{xc} - \mu_{xc}) \\ \tilde{E} &= E_{Bsv} + \int \rho_{sv} (\varepsilon_H - \mu_H + \varepsilon_{xc} - \mu_{xc}) + \int (\varepsilon_{Hv} + \varepsilon_{xc}) \rho_{sc} \\ E_F &= E_{Bsc} + \int \rho_{sc} (\varepsilon_H - \mu_H + \varepsilon_{xc} - \mu_{xc}) - \int (\varepsilon_{Hv} + \varepsilon_{xc}) \rho_{sc} \end{aligned}$$

In computing \tilde{E} as in Eq. (II C-6), three kinds of terms enter.

1. $E_{Bsv}^j = \sum_{nl}^{valence} \omega_{nl} \varepsilon_{nl}^j$
2. $E_{cv}^j = \int_0^\infty \rho_{sc}^j (\varepsilon_{Hv}^j + \varepsilon_{xc}^j) dr$
3. $E_{Hxc}^j = \int_0^\infty \rho_{sv}^j (\varepsilon_H^j + \varepsilon_{xc}^j - (\mu_H^{j-1} + \mu_{xc}^{j-1})) dr$

Taken together we call these Eq. (II C-7).

(I choose the names carefully to be suggestive of the variables in the FORTRAN programs.)

In the reference (to-be-frozen) AE calculation, save the following quantities: (assuming that the nth iteration is conv)

$$\rho_{sc}^{(n)}(r), E_{Bsv}^{(n)}, E_{cv}^{(n)}, E_{Hxc}^{(n)}, \tilde{E}^{(n)}, E_{TOT}^{(n)} \text{ and } V_{coul}^{(n)}(r) = \mu_H^{n-1}(r) + \mu_{xc}^{n-1}(r).$$

{It is interesting (Ref. 5) that quantities 1, 2, and 3 named above will separately have first order convergence in errors $\Delta\rho(r)$ while their sum (the total energy) has only errors $\propto (\Delta\rho(r))^2$.}

Then in FC calculation, only compute the \tilde{E} part, leaving out core terms.

$$E_{TOT}^{(FC)} = \overbrace{(E_{TOT}^{(AE)}(ref) - \tilde{E}_{ref})}^{E_F} + \tilde{E}^{FC}$$

or the change in E_{TOT} is simply $\tilde{E}^{(FC)} - \tilde{E}^{(AE)}$.

I generally denote the electron screening or coulomb part of $V(r)$, made up simply of Hartree + excorr, as

$$V_{coul}^{(j)}(r) \equiv \mu_H^{(j-1)}(r) + \mu_{xc}^{(j-1)}(r) \quad (\text{II C-8})$$

Then the contribution $E_{Hxc}^{(i)} = \int \rho_{sv}^{(i)} \left(\varepsilon_H^{(i)} + \varepsilon_{xc}^{(i)} - V_{coul}^{(i)}(r) \right) dr$.

To keep the frozen core calculations variationally correct, I save $V_{coul}^{(n)}(r)$ along with $\rho_{sc}^{(n)}(r)$. This is all performed automatically in HFSE and SCPOTD.

Aside regarding accelerated convergence:

Convergence in the self-consistent screening term V_{coul} is improved by various schemes which mix values from different iterations. My programs incorporate ‘‘Pratt accelerated convergence’’ (Ref. 8). This generally takes a form

$$V_{coul}^{(j)}(r) = \alpha(r) \left[\mu_H^{(j-1)}(r) + \mu_{xc}^{(j-1)}(r) \right] + (1 - \alpha(r)) V_{coul}^{(j-1)}(r) \quad (\text{II C-9})$$

where $0 \leq \alpha(r) \leq 0.5$ and $\alpha(r)$ is optimized in some way. I can still use

$$E_{TOT}^{(j)} = E_{Bs}^{(j)} + \int \rho_s^{(j)} \left(\varepsilon_H^{(j)} + \varepsilon_{xc}^{(j)} - V_{coul}^{(j)} \right) dr$$

and be variationally correct. If $v(r)$ is the nuclear potential on core psp, then for the first iteration I use

$$V_{COUL}^{(1)}(r) \equiv V_{SCREENED}^{(1)} - v(r)$$

for whatever screened starting $v(r)$ is given.

3 Numerical details

Kleinman psp \rightarrow PRL 48, 1425(1982).

HSC:

$$\hat{V}_{SL} = \sum_l |Y_{l0} \rangle \delta V_l(r) \langle Y_{l0}|$$

KB:

$$\hat{V}_{NL} = \sum_l \frac{|\delta V_l \psi_l Y_{l0} \rangle \langle Y_{l0} \psi_l \delta V_l|}{\langle Y_{l0} \psi_l | \delta V_l | Y_{l0} \psi_l \rangle}$$

$\psi_l =$ atomic pseudowf

$\psi_{nlm} = \psi_{nl}(r) Y_{lm}(\theta, \phi)$

$$\langle q | V_{SL} | q' \rangle = \sum_l 4\pi(2l+1) P_l(\cos \theta_{qq'}) \int_0^\infty r^2 dr j_l(2\pi qr) j_l(2\pi q' r) \delta V_l(r)$$

$$\begin{aligned} \langle q | V_{NL} | q' \rangle &= \sum_l 4\pi(2l+1) P_l(\cos \theta_{qq'}) \left(\int_0^\infty r^2 dr j_l(2\pi qr) \psi_l(r) \delta V_l(r) \right) \\ &\otimes \left(\int_0^\infty r^2 dr j_l(2\pi q' r) \psi_l(r) \delta V_l(r) \right) / \left(\int_0^\infty r^2 dr (\psi_l(r))^2 \delta V_l(r) \right) \\ &= \sum_l 4\pi(2l+1) P_l(\cos \theta_{qq'}) f_l(|q|) f_l(|q'|) / \eta_l \end{aligned}$$

$$P_0(x) = 1 \quad P_1(x) = x \quad P_2(x) = \frac{1}{2}(3x^2 - 1) \quad \cos \theta_{qq'} = \frac{q \cdot q'}{|q||q'|}$$

$$\begin{aligned}
P_2(\cos \theta_{qq'}) &= \frac{1}{2} (3 \cos^2 \theta_{qq'} - 1) & \cos \theta_{qq'} &= \frac{q \cdot q'}{|q| |q'|} \\
&= \frac{1}{2} \left(3 \left(\frac{q \cdot q'}{qq'} \right)^2 - 1 \right)
\end{aligned}$$

$$\begin{aligned}
(q \cdot q')^2 &= \left(\sum_i q_i q'_i \right)^2 \\
&= (q_1 q'_1)^2 + (q_2 q'_2)^2 + (q_3 q'_3)^2 + 2(q_1 q_2 q'_1 q'_2 + q_2 q_3 q'_2 q'_3 + q_3 q_1 q'_3 q'_1)
\end{aligned}$$

Assuming \vec{q} in cartesian coordinates (otherwise need G^{metric}):

$l = 0$:

$$\frac{4\pi}{\eta_0} f_0(q) f_0(q')$$

$l = 1$:

$$\frac{12\pi}{\eta_1} \left(f_1(|q|) \frac{\vec{q}}{|q|} \cdot f_1(|q'|) \frac{\vec{q}'}{|q'|} \right)$$

$l = 2$:

$$\frac{20\pi}{\eta_2} \cdot \frac{3}{2} \left(\sum_{ij} f_2(|q|) \frac{q_i q_j}{|q|^2} \cdot f_2(|q'|) \frac{q'_i q'_j}{|q'|^2} \right) - \frac{20\pi}{\eta_2} \cdot \frac{1}{2} (f_2(|q|) f_2(|q'|))$$

These could be computed in atomic programs on a standard radial grid:

$$\begin{aligned}
\eta_l &\equiv \int_0^\infty r^2 dr (\psi_l(r))^2 \delta V_l(r) \\
f_l(q) &\equiv \int_0^\infty r^2 dr j_l(2\pi qr) \psi_l(r) \delta V_l(r)
\end{aligned}$$

$\sum_{q'} V(q, q') \psi(q')$ requires

$l = 0 :$

$$\sum_{q'} f_0(|q'|) \psi(q')$$

$l = 1 :$

$$\sum_{q'} f_1(|q'|) \left(\frac{(q')_\mu}{|q'|} \right) \psi(q') \quad 3 \text{ terms}$$

$l = 2 :$

$$\sum_{q'} f_2(|q'|) \left(\frac{(q')_\mu (q')_\nu}{|q'|^2} \right) \psi(q') \quad 6 \text{ terms}$$

and

$$\sum_{q'} f_2(|q'|) \psi(q')$$

for every n, k .

Each l has only one function:

$$f_l(q) = \int_0^\infty r^2 dr j_l(2\pi qr) \psi_l(r) \delta V_l(r)$$

where $\psi_l(r)$ is atomic pseudo wf in reference state.

Roberto Car, prior to the rediscovery of the Kleinman-Bylander form described above, had suggested replacing the radial integrals with a quadrature sum with as few terms as possible:

$$\int_0^\infty r^2 dr j_l(2\pi qr) j_l(2\pi q' r) \delta V_l(r) \simeq \sum_n \omega_n r_n^2 j_l(2\pi q r_n) j_l(2\pi q' r_n) \delta V_l(r_n)$$

would need $\sum_{q'} j_l(2\pi r_n q') \psi(q')$ for each n, l .

$l = 0 :$

$$4\pi \sum_n \omega_n r_n^2 \delta V_0(r_n) j_0(2\pi r_n q) \sum_{q'} j_0(2\pi r_n q') \psi(q')$$

$l = 1 :$

$$12\pi \sum_n \omega_n r_n^2 \delta V_1(r_n) j_1(2\pi r_n q) \frac{\vec{q}}{|q|} \cdot \sum_{q'} j_1(2\pi r_n q') \frac{\vec{q}'}{|q'|} \psi(q')$$

KB removes necessity for \sum_n and storage thereof.

If not separable:

$$\sum_{q'} \langle q | V_{SL} | q' \rangle \psi(q') = \sum_l 4\pi(2l+1) \sum_{q'} P_l(\cos \theta_{qq'}) \overbrace{\int_0^\infty r^2 dr j_l(2\pi qr) j_l(2\pi q'r) \delta V_l(r)}^{\delta \tilde{V}_l(q, q')} \psi(q')$$

$l = 0 :$

$$4\pi \sum_{q'} \delta \tilde{V}_{l=0}(q, q') \psi(q')$$

$l = 1 :$

$$12\pi \frac{\vec{q}}{|q|} \cdot \sum_{q'} \delta V_1(q, q') \psi(q') \frac{\vec{q}'}{|q'|}$$

Nonlocal operator in real space: (spherically symmetric atom)

$$\hat{V}_{NL} \psi_l(r) = \frac{\int_0^\infty \psi_l^0(r') \delta V(r') \psi_l(r') dr'}{\int_0^\infty \psi_l^0(r') \delta V(r') \psi_l^0(r') dr'} \psi_l^0(r) \delta V(r)$$

Hence $\hat{V}_{NL} \psi_l^0(r) =: \delta V_l(r) \psi_l^0(r)$, reduces to HSC.

Norm-conserving psp transferability:

(all-el, atomic units)

$$\begin{aligned} & -\frac{1}{2} \frac{d^2 \psi}{dr^2} + \frac{1}{2} \frac{l(l+1)}{r^2} \psi + V \psi - \varepsilon \psi = 0 \\ \Rightarrow & \frac{\psi''}{\psi} = \frac{d^2 \ln \psi}{dr^2} + \left(\frac{d \ln \psi}{dr} \right)^2 = \frac{l(l+1)}{r^2} + 2(V(r) - \varepsilon) \\ \Rightarrow & \frac{d}{d\varepsilon} \left(\frac{d^2 \ln \psi}{dr^2} + \left(\frac{d \ln \psi}{dr} \right)^2 \right) = \frac{1}{\psi^2} \frac{d}{dr} \left(\psi^2 \frac{d}{d\varepsilon} \frac{d \ln \psi}{dr} \right) = -2 \end{aligned}$$

$$\Rightarrow \psi^2(R) \frac{d}{d\varepsilon} \frac{d \ln \psi}{dr} \Big|_R = -2 \int_0^R \psi^2 dr$$

Psp

$$-\frac{1}{2} \frac{d^2 \psi}{dr^2} + \frac{1}{2} \frac{l(l+1)}{r^2} \psi + V_{local}(r) \psi(r) + \hat{V}_{NL} \psi(r) - \varepsilon \psi = 0$$

$$\frac{\psi''}{\psi} = \frac{l(l+1)}{r^2} + 2 \left(V(r) + \frac{\hat{V}_{NL} \psi(r)}{\psi(r)} - \varepsilon \right)$$

$$\frac{d}{d\varepsilon} \left(\frac{\psi''}{\psi} \right) = 2 \left(-\frac{1}{\psi^2} \frac{d\psi}{d\varepsilon} \hat{V}_{NL} \psi(r) + \frac{1}{\psi(r)} \frac{d}{d\varepsilon} \left(\hat{V}_{NL} \psi(r) \right) - 1 \right)$$

$$\frac{d}{d\varepsilon} \left(\hat{V}_{NL} \psi(r) \right) = \frac{\int_0^\infty \psi^0(r') \delta V(r') \frac{d\psi(r')}{d\varepsilon} dr'}{\int_0^\infty \psi^0 \delta V \psi^0} \psi^0(r) \delta V(r)$$

$$\frac{1}{\psi^2} \frac{d}{dr} \left(\psi^2 \frac{d}{d\varepsilon} \frac{d \ln \psi}{dr} \right) = -2 \left(1 + \frac{1}{\psi^2} \frac{d\psi}{d\varepsilon} \frac{\int_0^\infty \psi^0 \delta V \psi}{\int_0^\infty \psi^0 \delta V \psi^0} \psi^0(r) \delta V(r) - \frac{1}{\psi(r)} \frac{\int_0^\infty \psi^0 \delta V \frac{d\psi}{d\varepsilon}}{\int_0^\infty \psi^0 \delta V \psi^0} \psi^0(r) \delta V(r) \right)$$

$$\begin{aligned} \psi^2 \frac{d}{d\varepsilon} \frac{d \ln \psi}{dr} \Big|_R &= -2 \int_0^R \psi^2(r) dr \\ &- 2 \left\{ \int_0^\infty \psi^0(r') \delta V(r') \psi(r') dr' \int_0^R \psi^0(r') \delta V(r') \frac{d\psi(r')}{d\varepsilon} dr' \right. \\ &\quad \left. - \int_0^\infty \psi^0(r') \delta V(r') \frac{d\psi(r')}{d\varepsilon} dr' \int_0^R \psi^0 \delta V \psi \right\} \\ &\quad / \int_0^\infty \psi^0 \delta V \psi^0 \end{aligned}$$

By construction $\delta V(r) \rightarrow 0$ for $R > r_c$, which is where $\psi^{PS}(r) = \psi^{all-el}(r)$ etc.

Hence additional terms add to 0 for $R > r_c$.

∴ Kleinman-Bylander psp is equally transferable.

$$L = \frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_{GG'} C_{Gnk}^* C_{G'nk} \sum_{\alpha} e^{-2\pi i \tau_{\alpha} \cdot (G-G')} V_{\alpha}(k+G, k+G')$$

$\omega(k)$ is the weight of the k -pt for Brillouin zone summation.

$$\begin{aligned} V_{\alpha}(k+G, k+G') &= \frac{4\pi}{\eta_0^{\alpha}} f_0^{\alpha}(|k+G|) f_0^{\alpha}(|k+G'|) \\ &+ \frac{12\pi}{\eta_1^{\alpha}} \frac{(\vec{k} + \vec{G}')}{|k+G|} f_1^{\alpha}(|k+G|) \cdot \frac{(\vec{k} + \vec{G}')}{|k+G'|} f_1^{\alpha}(|k+G'|) \\ &+ \frac{20\pi}{\eta_2^{\alpha}} \left[\frac{3}{2} \left(\sum_{ijkl} \frac{(k+G)_i (k+G)_j}{|k+G|^2} f_2^{\alpha}(|k+G|) \frac{(k+G')_k (k+G')_l}{|k+G'|^2} f_2^{\alpha}(|k+G'|) \right) \right. \\ &\quad \left. - \frac{1}{2} f_2^{\alpha}(|k+G|) f_2^{\alpha}(|k+G'|) \right] \end{aligned}$$

(Last term is 0 if $V_{LOCAL} = V_{l=2} \Rightarrow \delta V_{l=2} = 0$, or if $l = 2$ not included)

$$\frac{\partial E_{NL}}{\partial C_{Gnk}^*} = \frac{\omega(k)}{\Omega_0} \sum_{G'} \sum_{\alpha=1}^{NATOMS} e^{-2\pi i \vec{\tau}_{\alpha} \cdot (\vec{G}-\vec{G}')} V_{\alpha}(k+G, k+G') C_{G'nk} \times 2$$

$$g_0^{\alpha}(n, k) \equiv \sum_{G'} e^{2\pi i \tau_{\alpha} \cdot G'} f_0^{\alpha}(|k+G'|) C_{G'nk}$$

$$g_1^{\alpha}(n, k, \mu) \equiv \sum_{G'} e^{2\pi i \tau_{\alpha} \cdot G'} f_1^{\alpha}(|k+G'|) C_{G'nk} \frac{(k+G')_{\mu}}{|k+G'|}$$

$$g_2^{\alpha}(n, k, \mu, \nu) \equiv \sum_{G'} e^{2\pi i \tau_{\alpha} \cdot G'} f_2^{\alpha}(|k+G'|) C_{G'nk} \frac{(k+G')_{\mu} (k+G')_{\nu}}{|k+G'|^2}$$

$$g^{\alpha}(n, k) \equiv \sum_{G'} e^{2\pi i \tau_{\alpha} \cdot G'} f_2^{\alpha}(|k+G'|) C_{G'nk}$$

$$\frac{\partial E_{NL}(l=0)}{\partial C_{Gnk}^*} = \frac{\omega(k)}{\Omega_0} (4\pi) \sum_{\alpha=1}^{NATOMS} e^{-2\pi i G \cdot \tau_\alpha} f_0^\alpha(|k+G|) g_0^\alpha(nk) / \eta_0^\alpha$$

$$\frac{\partial E_{NL}(l=1)}{\partial C_{Gnk}^*} = \frac{\omega(k)}{\Omega_0} (12\pi) \sum_{\alpha} e^{-2\pi i G \cdot \tau_\alpha} \sum_{\mu\nu} \frac{(k+G)_\mu}{|k+G|} f_1^\alpha(|k+G|) G_{\mu\nu}^{metric} g_1^\alpha(n, k, \nu) / \eta_1^\alpha$$

$$\begin{aligned} \frac{\partial E_{NL}(l=2)}{\partial C_{Gnk}^*} &= \frac{\omega(k)}{\Omega_0} (20\pi) \sum_{\alpha} e^{-2\pi i G \cdot \tau_\alpha} \\ &\left(\frac{3}{2} \sum_{\mu\nu\lambda\delta} \frac{(k+G)_\mu (k+G)_\nu}{|k+G|^2} f_2^\alpha(|k+G|) G_{\mu\lambda}^{metric} G_{\nu\delta}^{metric} g_2^\alpha(n, k, \lambda, \delta) \right. \\ &\quad \left. - \frac{1}{2} f_2^\alpha(|k+G|) g^\alpha(nk) \right) / \eta_2^\alpha \end{aligned}$$

For k in reduced coordinates,

$$\begin{aligned} \vec{k} \cdot \vec{k}' &\equiv \sum_{\mu, \nu=1}^3 k_\mu G_{\mu\nu}^{met} k'_\nu \\ G_{\mu\nu}^{met} &\equiv \vec{G}_\mu^p \cdot \vec{G}_\nu^p \\ \vec{G}_\mu^p &\equiv \text{reciprocal lattice primitive translation} \end{aligned}$$

3.1 Coordinate derivatives

$\vec{\tau}_\alpha$ = atom location in terms of primitive transl. $\vec{R}_1^P, \vec{R}_2^P, \vec{R}_3^P$.

$$\begin{aligned} E_{NL}(l=0) &= \frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_{\alpha} \frac{4\pi}{\eta_0^\alpha} (g_0^\alpha(nk))^* (g_0^\alpha(nk)) \\ \left(\frac{\partial E_{NL}(l=0)}{\partial \tau_{\alpha\mu}} \right) &= \frac{4\pi}{\eta_0^\alpha \Omega_0} \sum_{n,k} \frac{\omega(k)}{2} 2\text{Re} \left((g_0^\alpha(nk))^* \frac{\partial g_0^\alpha(nk)}{\partial \tau_{\alpha\mu}} \right) \\ \left(\frac{\partial g_0^\alpha(nk)}{\partial \tau_{\alpha\mu}} \right) &= \sum_G (2\pi i G_\mu) e^{2\pi i \vec{\tau}_\alpha \cdot \vec{G}} f_0^\alpha(|k+G|) C_{Gnk} \end{aligned}$$

G_μ is also in reduced coords.

Similarly for $l = 1$,

$$E_{NL}(l = 1) = \frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_{\alpha} \frac{12\pi}{\eta_1^\alpha} \sum_{\mu, \nu=1}^3 (g_1^\alpha(n, k, \mu))^* G_{\mu\nu}^{met} (g_1^\alpha(n, k, \nu))$$

$$G_{\mu\nu}^{met} = \vec{G}_\mu^P \cdot \vec{G}_\nu^P$$

\vec{G}_μ^P = primitive reciprocal lattice vector; $\mu = 1, 2, 3$

eg in cubic cell $G^{met} = \frac{1}{a_0^2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

$$\frac{\partial g_1^\alpha(n, k, \mu)}{\partial \tau_{\alpha\lambda}} = \sum_G [2\pi i G_\lambda] e^{2\pi i G \cdot \tau_\alpha} f_1^\alpha(|k + G|) \frac{(k + G)_\mu}{|k + G|} C_{Gnk}$$

$$\left(\frac{\partial E_{NL}(l = 1)}{\partial \tau_{\alpha\lambda}} \right) = \frac{12\pi}{\eta_1^\alpha \Omega_0} \sum_{nk} \omega(k) 2Re \left[\sum_{\mu\nu} (g_1^\alpha(nk\mu))^* G_{\mu\nu}^{met} \frac{\partial g_1^\alpha(nk\nu)}{\partial \tau_{\alpha\lambda}} \right]$$

For $l = 2$,

$$E_{NL}(l = 2) =$$

$$\frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_{\alpha} \frac{20\pi}{\eta_2^\alpha} \left[\frac{3}{2} \sum_{ijkl} (g_2^\alpha(nkij))^* G_{ik}^{met} G_{jl}^{met} (g_2^\alpha(nkkl)) - \frac{1}{2} (g^\alpha(nk))^* (g^\alpha(nk)) \right]$$

$$\frac{\partial g_2^\alpha(nkij)}{\partial \tau_{\alpha\lambda}} = \sum_G [2\pi i G_\lambda] e^{2\pi i \vec{G} \cdot \vec{\tau}_\alpha} f_2^\alpha(|k + G|) \frac{(k + G)_i (k + G)_j}{|k + G|^2} C_{Gnk}$$

$$\frac{\partial g^\alpha(nk)}{\partial \tau_{\alpha\lambda}} = \sum_G [2\pi i G_\lambda] e^{2\pi i G \cdot \tau} f_2^\alpha(|k + G|) C_{Gnk}$$

$$\frac{\partial E_{NL}(l=2)}{\partial \tau_{\alpha\lambda}} = \frac{20\pi}{\eta_2^\alpha \Omega_0} \sum_{nk} \omega(k) 2Re \left[\frac{3}{2} \sum_{ijlp} (g_2^\alpha(nkij))^* G_{il}^{met} G_{jp}^{met} \frac{\partial g_2^\alpha(n, k, l, p)}{\partial \tau_{\alpha\lambda}} - \frac{1}{2} (g^\alpha(nk))^* \frac{\partial g^\alpha(nk)}{\partial \tau_{\alpha\lambda}} \right]$$

If special k points are used then $\frac{\partial E_{NL}}{\partial \tau_{\alpha\mu}}$ must be symmetrized. Let S express the symmetry operation in terms of the primitive translations \vec{R}_μ^P .

Define atom $S^T(\alpha)$ by $\vec{\tau}_{S^T(\alpha)} \equiv S^T(\vec{\tau}_\alpha - \vec{\tau}_{nonsymorphic}) + \vec{R}_{transl.}$

It can be shown that

$$\boxed{\left(\frac{\partial E_{NL}}{\partial \tau_{\alpha\mu}} \right)_{symmetrized} = \frac{1}{N_{symm}} \sum_S S_{\mu\nu} \left(\frac{\partial E_{NL}}{\partial \tau_{S^T(\alpha)}} \right)_{unsymm}}$$

3.2 Length scale derivatives

a_λ = length scale of primitive cell translations \vec{R}_λ^P , $\lambda = 1, 2, 3$.

Reciprocal lattice primitive vectors can be written $\vec{G}_\lambda^P = \vec{g}_\lambda / a_\lambda$ where \vec{g}_λ is dimensionless.

Hence the reciprocal space metric is $G_{\mu\nu} = \vec{g}_\mu \cdot \vec{g}_\nu / a_\mu a_\nu$.

The cartesian coordinates of \vec{k} are

$$\vec{k}^C = k_1 \vec{g}_1 / a_1 + k_2 \vec{g}_2 / a_2 + k_3 \vec{g}_3 / a_3$$

where $\vec{k} = (k_1, k_2, k_3)$ in reduced units.

$$|k|^2 = \vec{k}^C \cdot \vec{k}^C = \sum_{\mu\nu} k_\mu k_\nu G_{\mu\nu}$$

In terms of \vec{k} and $G_{\mu\nu}$, taking into account that

$$\frac{\partial G_{\mu\nu}}{\partial a_\lambda} = -\frac{G_{\mu\nu}}{a_\lambda} (\delta_{\mu\lambda} + \delta_{\nu\lambda})$$

the derivatives of $|k|^2$ wrt length scale a_λ is

$$\begin{aligned}\frac{\partial |k|^2}{\partial a_\lambda} &= -\frac{2}{a_\lambda} k_\lambda \sum_\nu G_{\lambda\nu} k_\nu. \\ \Rightarrow \frac{\partial |k|}{\partial a_\lambda} &= -\frac{1}{a_\lambda} \frac{k_\lambda}{|k|} \sum_\nu G_{\lambda\nu} k_\nu.\end{aligned}$$

$$\begin{aligned}\frac{\partial E_{NL}(l=0)}{\partial a_\lambda} &= -\frac{E_{NL}(l=0)}{a_\lambda} + \frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_\alpha \frac{4\pi}{\eta_0^\alpha} 2\text{Re} \left[(g_0^\alpha(nk))^* \frac{\partial g_0^\alpha(nk)}{\partial a_\lambda} \right] \\ \frac{\partial g_0^\alpha(nk)}{\partial a_\lambda} &= \sum_G e^{2\pi i G \cdot \tau_\alpha} f_0^{a'}(|k+G|) \frac{\partial |k+G|}{\partial a_\lambda} C_{Gnk}\end{aligned}$$

where the derivative $f_0^{a'}(|k+G|)$ is obtainable e.g. from spline fit to $f_0^a(|k+G|)$.

It is similar but messier for $l=1$.

$$\begin{aligned}\frac{\partial E_{NL}(l=1)}{\partial a_\lambda} &= -\frac{E_{NL}(l=1)}{a_\lambda} + \frac{1}{\Omega_0} \sum_{nk} \omega(k) \sum_\alpha \frac{12\pi}{\eta_1^\alpha} \times \\ &\quad \left\{ 2\text{Re} \left[\sum_{\mu\nu} g_1^{\alpha*}(nk\mu) G_{\mu\nu} \frac{\partial g_1^\alpha(nk\nu)}{\partial a_\lambda} \right] - \right. \\ &\quad \left. \frac{2}{a_\lambda} \text{Re} \left[\sum_\nu g_1^{\alpha*}(nk\lambda) G_{\lambda\nu} g_1^\alpha(nk\nu) \right] \right\}\end{aligned}$$

(last term uses $\frac{\partial G_{\mu\nu}}{\partial a_\lambda} = -\frac{G_{\mu\nu}}{a_\lambda} (\delta_{\mu\lambda} + \delta_{\nu\lambda})$ and $G_{\mu\nu} = G_{\nu\mu}$.)

$$\begin{aligned}\frac{\partial g_1^\alpha}{\partial a_\lambda} &= \sum_G e^{2\pi i \tau_\alpha \cdot G} \left\{ f_1^{\alpha'}(|k+G|) \frac{\partial |k+G|}{\partial a_\lambda} C_{Gnk} \frac{(k+G)_\mu}{|k+G|} \right. \\ &\quad \left. - f_1^\alpha(|k+G|) C_{Gnk} \frac{(k+G)_\mu}{|k+G|^2} \frac{\partial |k+G|}{\partial a_\lambda} \right\}\end{aligned}$$

$l=2$ is left as an exercise (!).

Symmetrizing $\frac{\partial E_{NL}}{\partial a_\lambda}$ in general for a special \vec{k} point scheme is also a little messy.