computing

betas and qs

for

NCPP/USPP/PAW
PseudoPotentials

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr) dr$$

Periodic potential

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$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \quad \sum_R \frac{\exp(-iG(R + \tau_s))}{N\Omega}$$

$$\mathcal{V} = N\Omega$$

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atomic form factor *crystal structure factor*

ab initio Norm Conserving PseudoPotentials

semilocal form

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

where $P_l(r,r') = \sum_m Y_{lm}(r)Y_{lm}^*(r')$ projects over $L^2 = l(l+1)$

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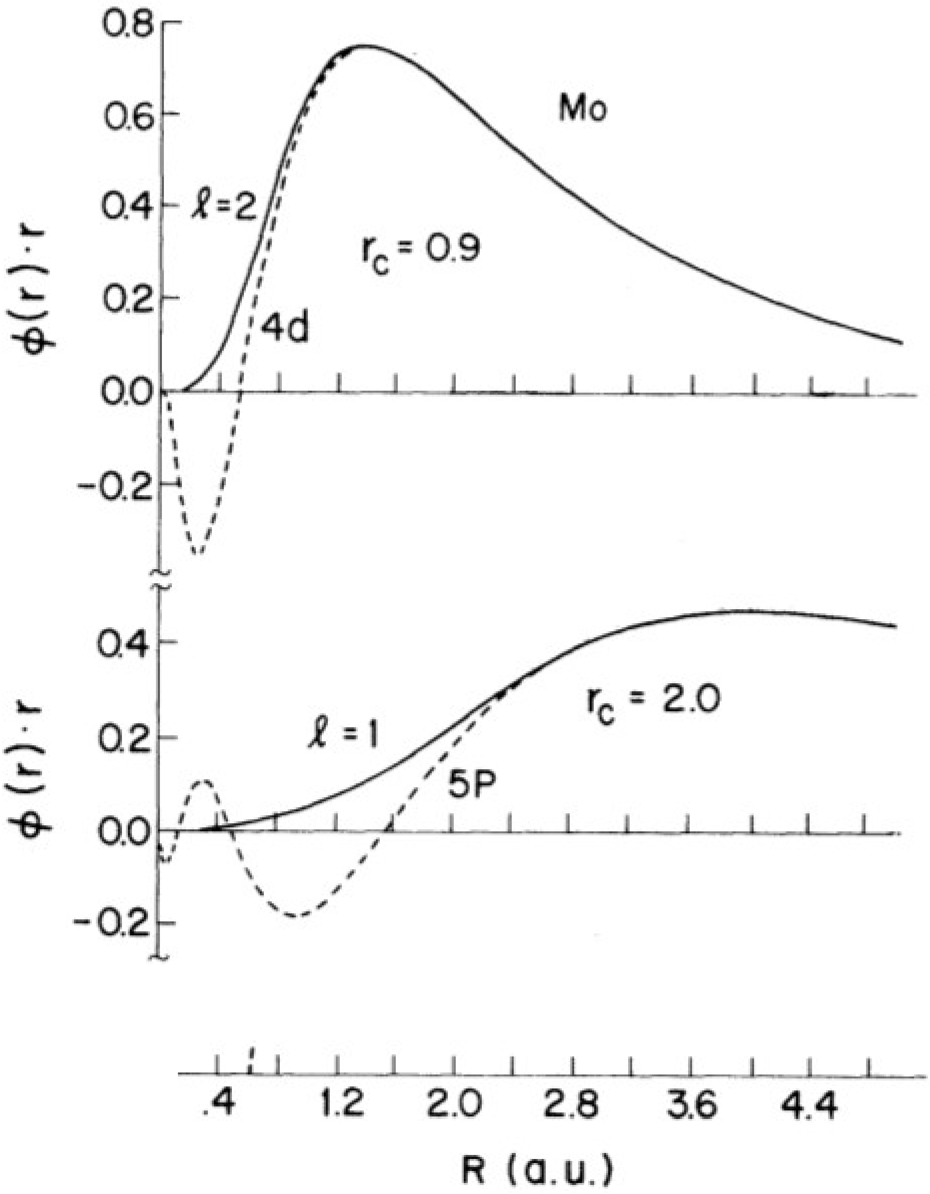
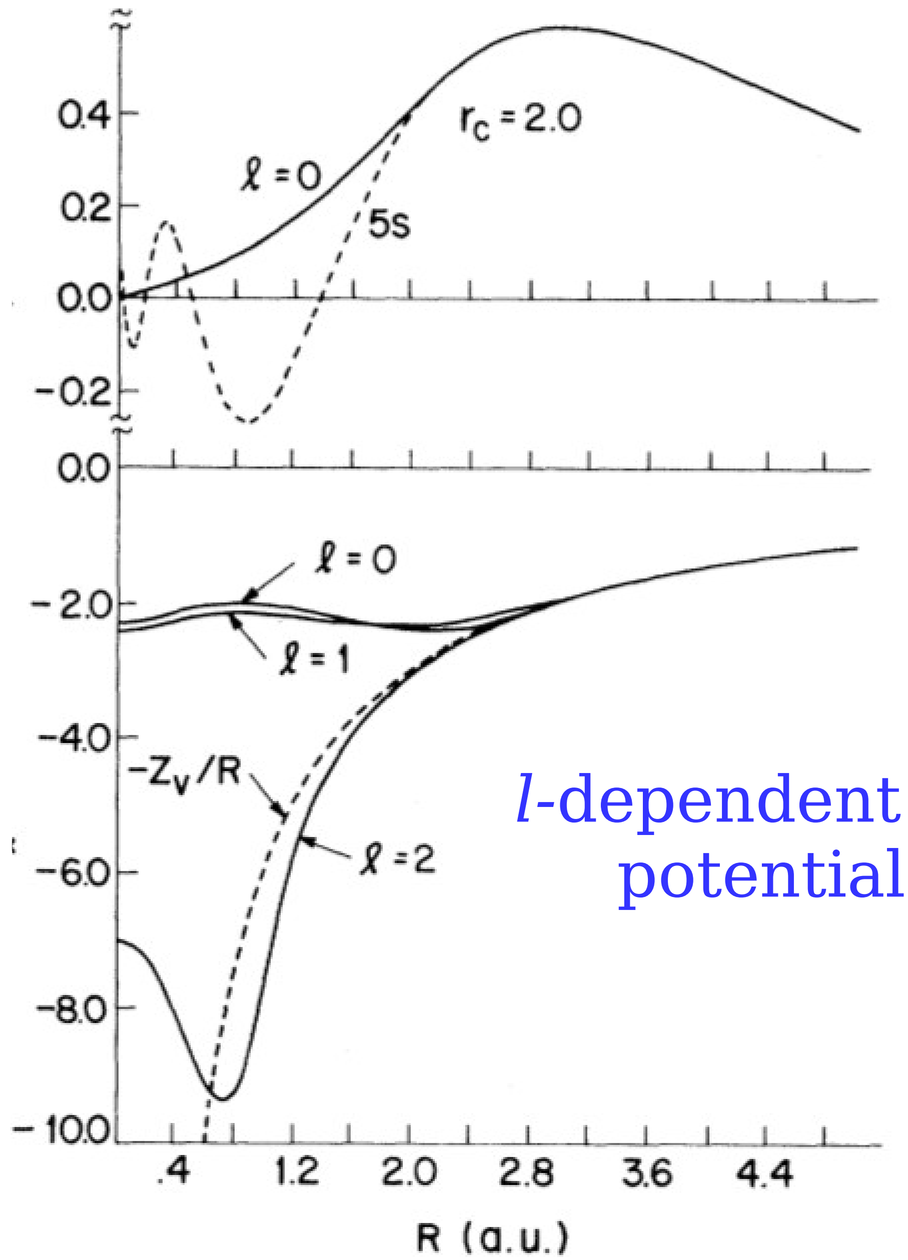
where $P_l(r,r') = \sum_m Y_{lm}(r)Y_{lm}^*(r')$ projects over $L^2 = l(l+1)$

$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\Delta V_l(|r|)$ is local in the radial coordinate, short ranged and l-dependent

An example: Mo





l-dependent potential

Hamann, schlueter & Chiang, *PRL* ***43****, 1494 (1979)*

An example: Mo

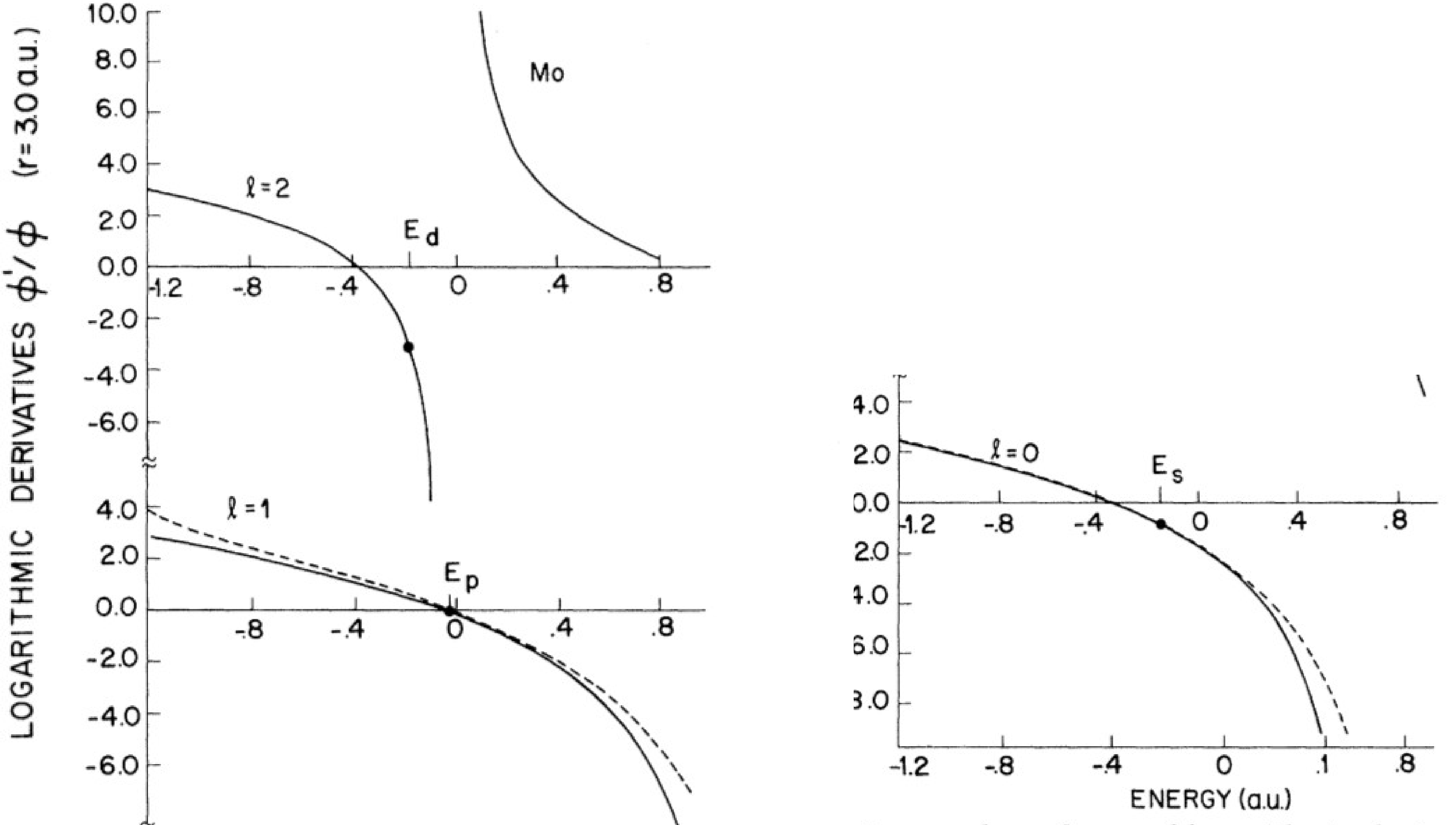


FIG. 2. Energy dependence of logarithmic derivatives at $r=3.0$ a.u. for Mo *ab initio* full-core atomic wave functions (broken lines) and pseudo wave functions (solid lines) as shown in Fig. 1.

Hamann, schlueter & Chiang,
PRL ***43****, 1494 (1979)*

ab initio Norm Conserving PseudoPotentials

- semilocal form

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

- Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle\; D_l\; \langle\beta_{lm}|r'\rangle$$

ab initio Norm Conserving PseudoPotentials

- semilocal form ...

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

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$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\langle r|\beta_{lm}\rangle = \Delta V_l(r)\phi_l(r)Y_{lm}(r)$ are localized radial functions such that the transformed pseudo acts in the same way as the original form on the reference config.

One has $D_l = \langle \phi_l|\Delta V_l|\phi_l\rangle^{-1}$

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

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ab initio Norm Conserving PseudoPotentials

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$$\tilde{V}_{Z_v}^{PS} = \textstyle\sum_{s,R} V_s^{loc}(|r - R - \tau_s|)\delta(r - r') + \displaystyle\sum_{s,R} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r - R - \tau_s|\beta_{lm}^s\rangle \ D_l^s \ \langle\beta_{lm}^s|r' - R - \tau_s\rangle$$

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \; D_l \; \langle \beta_{lm}|r'\rangle$$

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$$\langle k + G|\tilde{V}_{Z_v}^{PS}|k + G'\rangle = \sum\nolimits_s V_s^{loc}(|G - G'|) \; e^{-i(G-G')\tau_s} + \sum_{s} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle k + G|\beta_{lm}^s\rangle e^{-iG\tau_s} \; D_l^s \; e^{iG'\tau_s}\langle \beta_{lm}^s|k + G'\rangle$$

$$\langle \mathbf{r} | \beta_{nlm} \rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{r} | \beta_{nlm} \rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k} | \beta_{nlm} \rangle = \int \frac{e^{-i\mathbf{k}\mathbf{r}}}{\sqrt{\Omega}} \langle \mathbf{r} | \, \beta_{nlm} \rangle \, d\mathbf{r}$$

$$\langle \mathbf{r} | \beta_{nlm} \rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k} | \beta_{nlm} \rangle = \int \frac{e^{-i\mathbf{kr}}}{\sqrt{\Omega}} \langle \mathbf{r} | \ \beta_{nlm} \rangle \ d\mathbf{r}$$

$$exp[i\mathbf{kr}] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{r} | \beta_{nlm} \rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

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$$\langle \mathbf{k} | \beta_{nlm} \rangle = \frac{4\pi}{\sqrt{\Omega}} \ (-i)^l \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr \ \ Y_{lm}(\hat{\mathbf{k}})$$

$$\langle \mathbf{r}|\beta_{nlm}\rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

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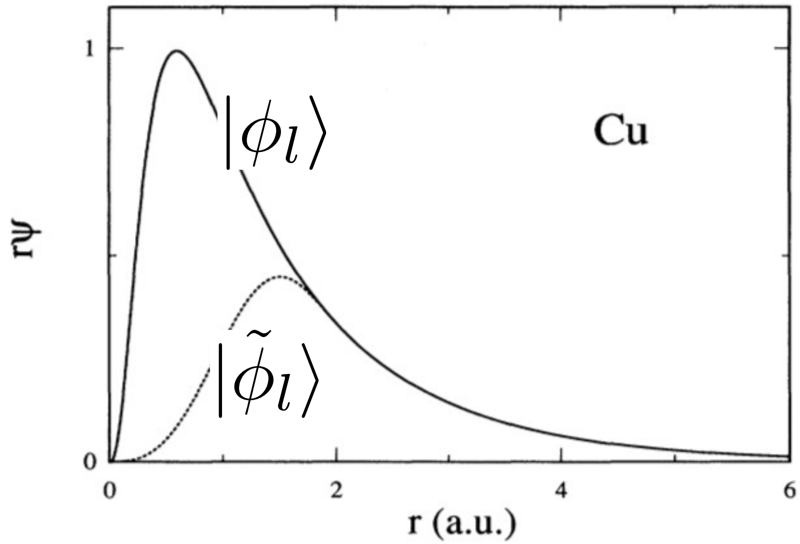
$$exp[i\mathbf{kr}] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \frac{4\pi}{\sqrt{\Omega}} (-i)^l \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr \ \ Y_{lm}(\hat{\mathbf{k}})$$

$$\boxed{\begin{gathered}\langle \mathbf{k}|\beta_{nlm}\rangle = (-i)^l\ \tilde{\beta}^{at}_{nl}(k)\ \ Y_{lm}(\hat{\mathbf{k}}) \\ \text{with} \quad \tilde{\beta}^{at}_{ln}(k) = \frac{4\pi}{\sqrt{\Omega}} \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr\end{gathered}}$$

Ultra Soft PseudoPotentials



$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{ll'} \langle \psi_i | \beta_l \rangle Q_{ll'}(r) \langle \beta_{l'} | \psi_i \rangle$$

where the "augmentation charges" are

$$Q_{ll'}(r) = \phi_l^*(r)\phi_l'(r) - \tilde{\phi}_l^*(r)\tilde{\phi}_l'(r)$$

$|\beta_l\rangle$ are projectors

$|\phi_l\rangle$ are atomic states (not necessarily bound)

$|\tilde{\phi}_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some *core radius*)

Ultra Soft PseudoPotentials

$$\hat{V}^{USPP} = V_{loc}(r) + \sum_{ll'} |\beta_l\rangle D^0_{ll'} \langle\beta_{l'}|$$

Orthogonality with USPP:

$$\langle\psi_i|S|\psi_j\rangle = \langle\psi_i|\psi_j\rangle + \sum_{ll'} \langle\psi_i|\beta_l\rangle q_{ll'} \langle\beta_{l'}|\psi_j\rangle = \delta_{ij}$$

where $$q_{ll'} = \int Q_{ll'}(r) dr$$

leading to a generalized eigenvalue problem

$$[H_{KS} - \varepsilon_i S] \; |\psi_i\rangle = 0$$

Ultra Soft PseudoPotentials

There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

$$E = \sum_i \langle \psi_i | \hat{T}_s + \hat{V}^{USPP} | \psi_i \rangle + E_{Hxc}[\rho] - \sum_{ij} \lambda_{ij} (\langle \psi_i | S | \psi_j \rangle - \delta_{ij})$$

where $$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{ll'} \langle \psi_i | \beta_l \rangle Q_{ll'}(r) \langle \beta_{l'} | \psi_i \rangle$$

$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_s \sum_i \sum_{ll'} \langle \psi_i | \beta_l^s \rangle Q_{ll'}(r - \tau_s) \langle \beta_{l'}^s | \psi_i \rangle$$

$$\rho(G) = \tilde{\rho}(G) + \sum_s \sum_{ll'} \sum_i \langle \psi_i | \beta_l^s \rangle \langle \beta_{l'}^s | \psi_i \rangle \; Q_{ll'}^s(G) e^{-iG\tau_s}$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega} \int e^{-i\mathbf{G}\mathbf{r}} Q_{nlm,n'l'm'}(\mathbf{r})\, d\mathbf{r}$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\; Y_{lm}(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{G}\mathbf{r}} Q_{nlm,n'l'm'}(\mathbf{r})\; d\mathbf{r}$$

$$Y_{lm}(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'} \alpha^{L}_{lm,l'm'}\; Y_{LM}(\hat{\mathbf{r}}), \qquad M = m + m'$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\ Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{Gr}} Q_{nlm,n'l'm'}(\mathbf{r})\ d\mathbf{r}$$

$$Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'} \alpha^{L}_{lm,l'm'}\ Y_{LM}(\hat{\mathbf{r}}), \qquad M = m + m'$$

$$exp[i\mathbf{Gr}] = 4\pi \sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(Gr) Y^*_{lm}(\hat{\mathbf{G}}) Y_{lm}(\hat{\mathbf{r}})$$

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$$Q_{nlm,n'l'm'}(\mathbf{G}) = \sum_{L=|l-l'|}^{l+l'} (-i)^L \alpha^{L}_{lm,l'm'} \;\; \tilde{Q}^{L}_{nl,n'l'}(G) \;\; Y_{Lm+m'}(\hat{\mathbf{G}})$$

with $\quad \tilde{Q}^{L}_{nl,n'l'}(G) = \frac{4\pi}{\Omega} \int_0^{\infty} j_L(Gr) \; \tilde{Q}^{at}_{nl,n'l'}(r) \; dr$

The betas and qs functions can be computed in reciprocal space as described above.

Alternatively they can be computed directly in real-space interpolating from the radial grid to the fft grid.

If the kinetic energy cutoff used is not converged enough the two procedure ARE NOT the same.

In our experience the G-space treatment is more relieable.