

1 Pseudopotential

plane wave: $\exp(i\mathbf{k} \cdot \mathbf{r}) = \sum_l (2l+1) i^l j_l(kr) P_l(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}})$

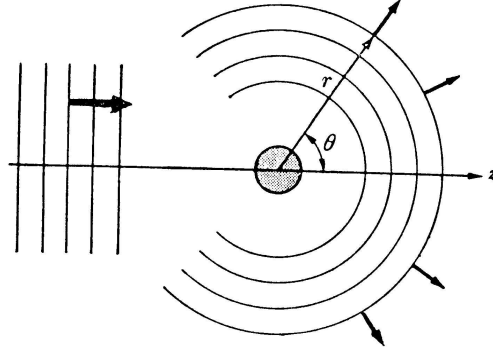


Figure 1: scattering of plane wave

the scattering amplitude

$$f(\theta) = (2ik)^{-1} \sum_l (2l+1) [\exp(2i\eta_l) - 1] P_l(\cos \theta) \quad (1)$$

the phase shift η_l

$$\eta_l = n_l \pi + \delta_l \quad (2)$$

n_l is an integer so $|\delta_l| < \pi/2$. We put

$$n_l = n - l - 1 \quad (3)$$

where n and l is the principal and angular quantum number of the wavefunction ψ_{nl} . $(n - l - 1)$ is the number of the nodes in the wavefunction ψ_{nl} , and corresponds to the number of the core states with angular momentum l . [eg. $3-2-1=0$ for 3d(no core d state), $4-0-1=3$ for 4s(core 1s, 2s, 3s state), $4-1-1=2$ for 4p(core 2p, 3p state)]

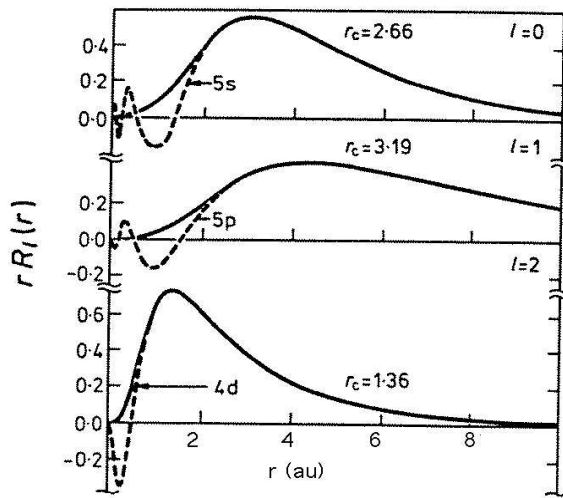


Figure 2: All electron and pseudowave functions of Mo atom

Pseudopotential: $n - l - 1 \Rightarrow 0$

The pseudo-wave function has no radical nodes, i.e. no rapid oscillations so that we expect a rapidly convergence series of plane wave.

For atom and ion system

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + V_H(r) + V_{xc}(r) - \epsilon_{nlm}\right)\psi_{nlm}(\mathbf{r}) = 0 \quad (4)$$

Here

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (5)$$

Logarithmic derivative

$$L_l \equiv (R'_l/R_l)|_{r=r_c} \quad (6)$$

The phase shift η_l can be obtained from the logarithmic derivative L_l

$$\tan \eta_l = \frac{j_l(kr_c)L_l - k j'_l(kr_c)}{n_l(kr_c)L_l - k n'_l(kr_c)} \quad (7)$$

In periodic potential if we replace the real potential inside the core sphere by a pseudopotential with the same scattering properties, then it also gives the same energy band structure.

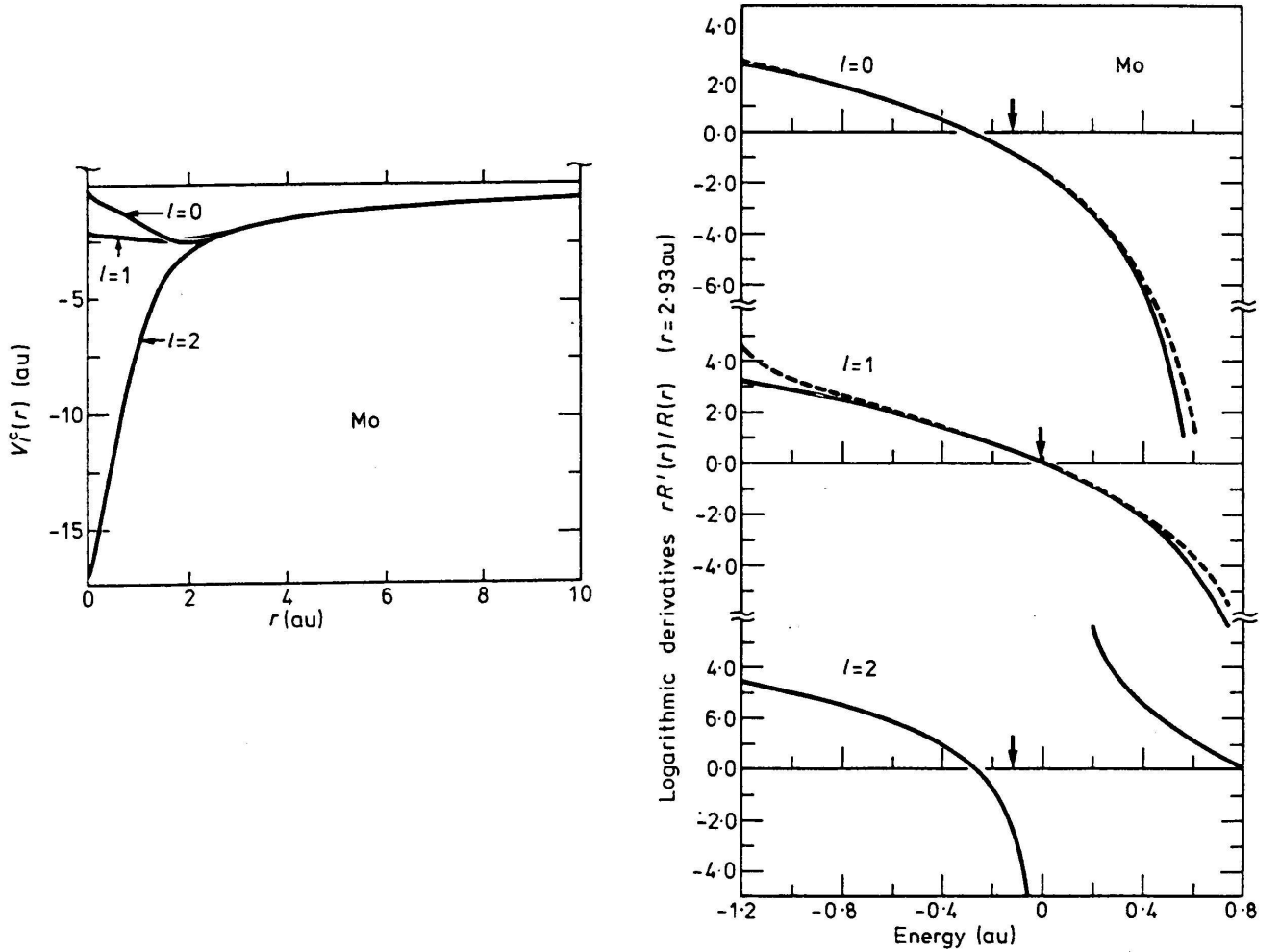


Figure 3: Pseudopotential and logarithmic derivative of all-electron and pseudo wave functions of Mo atom

$$\hat{v}_{ps} = \sum_l v_{ps,l}(r) \hat{P}_l \quad (8)$$

\hat{P}_l is projection operator that picks out l -th angular momentum component of the wavefunction so that $v_{ps,l}(r)$ acts only on that. (reference: M. L. Cohen and V. Heine, Ed. by H. Ehrenreich, F. Seitz and D. Turnbull, in: “*The fitting of pseudopotentials to experimental data and their subsequent application*”, (Academic, New York, 1970) p. 37-248.)

$\sum \hat{P}_l = 1$, then $\hat{v}_{ps} = v_{loc} + \sum_l (v_{ps,l} - v_{loc})$. If we put $v_{loc} = v_{ion,l=0}^{ps}$

$$\hat{v}_{ion}^{ps} \psi(\mathbf{r}) = \int d\mathbf{r}' v_{ion}^{ps}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \quad (9)$$

$$v_{ion}^{ps}(\mathbf{r}, \mathbf{r}') = v_0^{local}(r) \delta(\mathbf{r} - \mathbf{r}') + \sum_{l=1}^{l_{max}} (v_l^{ps}(r) - v_0^{local}(r)) 2\delta(r - r')/r'^2 \sum_m |Y_{lm}(\hat{\mathbf{r}})\rangle \langle Y_{lm}(\hat{\mathbf{r}}')| \quad (10)$$

$$\delta v_l^{nonlocal} = v_l^{ps} - v_0^{local} \quad (11)$$

Norm-Conserving Pseudopotentials (Hamman, Schlüter and Chiang, PRL, 43, 1494, 1979)

For real(all electron atom) and pseudoatom

(I) eigenvalues of the valence states are the same

(II) wavefunctions agree beyond a chosen core radius r_c .

(III) $\int_0^{r_c} dr r^2 4\pi \rho(r)$ agree \equiv **normconservation**. (The electrostatic potential produced outside r_c is identical for real and pseudo charge distributions.)

(IV) logarithmic derivatives and their energy derivatives agree. (scattering properties of the real ion cores are reproduced with minimum error as bonding and banding shifts eigenvalues away from the atomic levels.)

The properties (III) and (IV) are crucial for the pseudopotential transferability, and are related by a simple identity.

$$-\frac{1}{2} \frac{\partial}{\partial \epsilon} \frac{\partial}{\partial r} \ln R_l(r, \epsilon)|_{\epsilon=\epsilon_l, r=r_l^{cut}} = \frac{1}{(r_l^{cut} R_l(r_l^{cut}, \epsilon_l))^2} \int_0^{r_l^{cut}} dr r^2 R_l^2(r, \epsilon_l) \quad (12)$$

Derivation of logarithmic derivative(Harrison, Solid State Theory)

$$\epsilon R_l = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l + V(r) R_l + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} R_l \quad (13)$$

$$(\epsilon + \delta\epsilon) R'_l = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R'_l + V(r) R'_l + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} R'_l \quad (14)$$

If we apply R'_l to lhs of Eq.(13) and R_l to lhs of Eq.(14) and integral from 0 to R

$$-\delta\epsilon \int_0^R dr 4\pi r^2 R'_l R_l = -\frac{4\pi\hbar^2}{2m} \left(\int_0^R R'_l \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l - \int_0^R R_l \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R'_l \right) \quad (15)$$

Here we assume $V(r)$ had no ϵ dependence. Using partial integral

$$-\delta\epsilon \int_0^R dr 4\pi r^2 R'_l R_l = -\frac{4\pi\hbar^2}{2m} \left(\left[R'_l r^2 \frac{\partial R_l}{\partial r} \right]_0^R - \int_0^R dr \frac{\partial R'_l}{\partial r} r^2 \frac{\partial R_l}{\partial r} \right) \quad (16)$$

$$- \left[R_l r^2 \frac{\partial R'_l}{\partial r} \right]_0^R - \int_0^R dr \frac{\partial R_l}{\partial r} r^2 \frac{\partial R'_l}{\partial r} \right) \quad (17)$$

$$= -\frac{4\pi\hbar^2}{2m} \left(R_l' r^2 \frac{\partial R_l}{\partial r} - R_l r^2 \frac{\partial R_l'}{\partial r} \right)_R \quad (18)$$

$$R_l' = R_l + \frac{\partial R_l}{\partial \epsilon} \delta\epsilon \quad (19)$$

$$-\delta\epsilon \int_0^R dr 4\pi r^2 \left(R_l + \frac{\partial R_l}{\partial \epsilon} \delta\epsilon \right) R_l = -\frac{4\pi\hbar^2}{2m} \left(\left(R_l + \frac{\partial R_l}{\partial \epsilon} \delta\epsilon \right) r^2 \frac{\partial R_l}{\partial r} - R_l r^2 \frac{\partial \left(R_l + \frac{\partial R_l}{\partial \epsilon} \delta\epsilon \right)}{\partial r} \right)_R$$

$$-\delta\epsilon \int_0^R dr 4\pi r^2 \left(R_l^2 + R_l \frac{\partial R_l}{\partial \epsilon} \delta\epsilon \right) = -\frac{4\pi\hbar^2}{2m} \delta\epsilon \left(r^2 \frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - r^2 R_l \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right)_R \quad (20)$$

If we pick up the first-order of $\delta\epsilon$

$$\int_0^R dr r^2 R_l^2 = \frac{\hbar^2}{2m} R^2 \left(\frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - R_l \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right) \quad (21)$$

$$= \frac{\hbar^2}{2m} R^2 R_l^2 \left(R_l^{-2} \frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - R_l^{-1} \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right) \quad (22)$$

$$= -\frac{\hbar^2}{2m} R^2 R_l^2 \frac{\partial}{\partial \epsilon} \left(R_l^{-1} \frac{\partial R_l}{\partial r} \right) \quad (23)$$

$$= -\frac{\hbar^2}{2m} R^2 R_l^2 \frac{\partial}{\partial \epsilon} \frac{\partial}{\partial r} \ln R_l \quad (24)$$

$$(25)$$

Troullier and Martins(Kerker) Pseudopotential

$$v_{ion,l}^{ps}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2r R_l^{ps}} \frac{d^2}{dr^2} (r R_l^{ps}) - v_H^{ps} - v_{xc}^{ps} \quad (26)$$

$$R_l^{ps}(r) = r^l \exp[p(r)], \quad r \leq r_l^{cut} \quad (27)$$

where $p(r)$ is a polynomial of order six in r^2 .

For nonbound states **Hamman's generalized normconserving pseudopotential** is used.