Pseudopotentials

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How to abstract atoms in solid?

Background: Atomic Orbitals

$$\begin{cases} n = 1,2,\cdots \\ l \in [0, n-1] \\ m \in [-l, l] \end{cases}$$

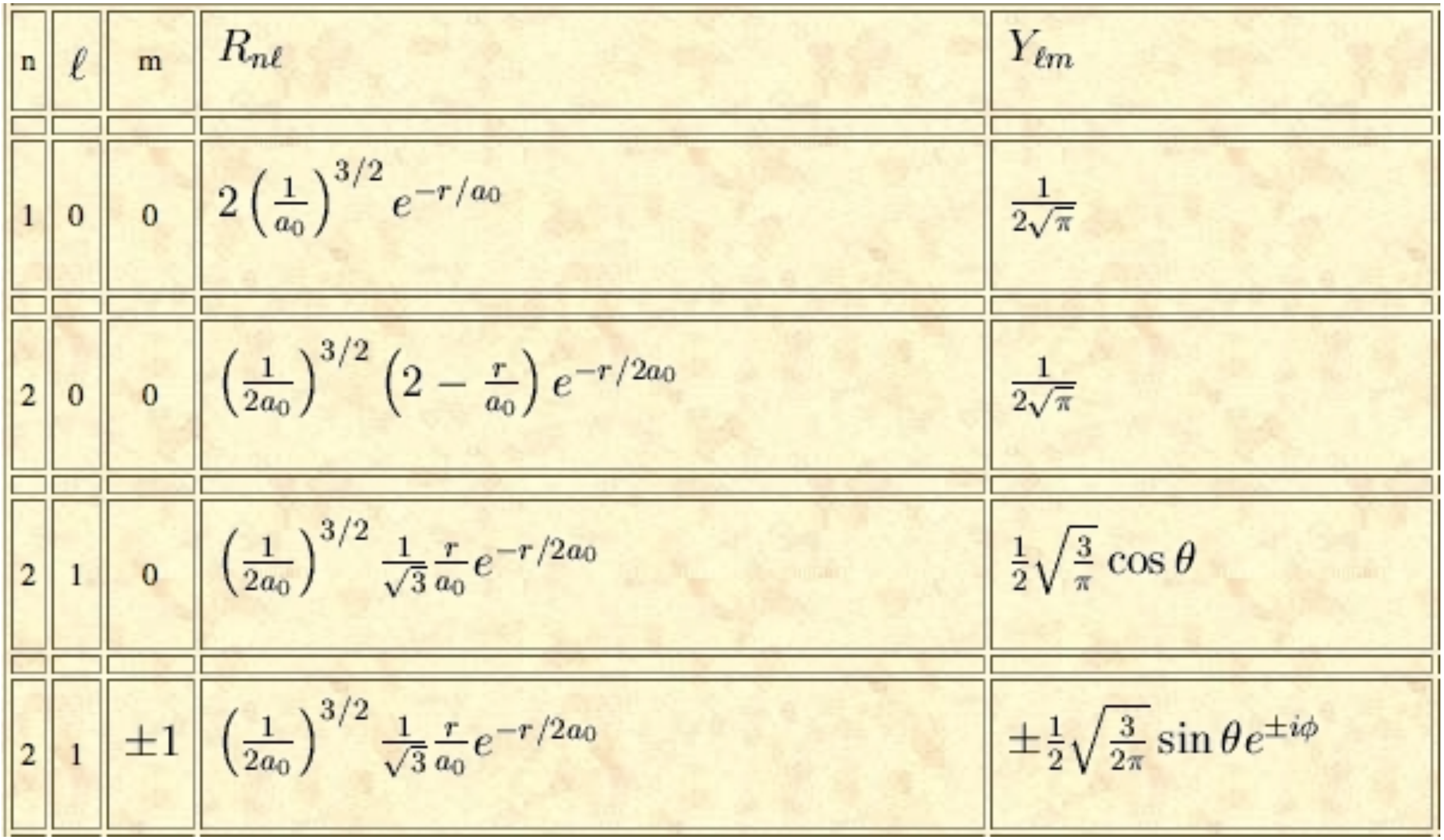
$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi)$$

Radial function

Spherical harmonics

s: $l = 0$
p: $l = 1$
d: $l = 2$

- **Hydrogen eigenstates ($\rho = v_{xc} = 0$)**

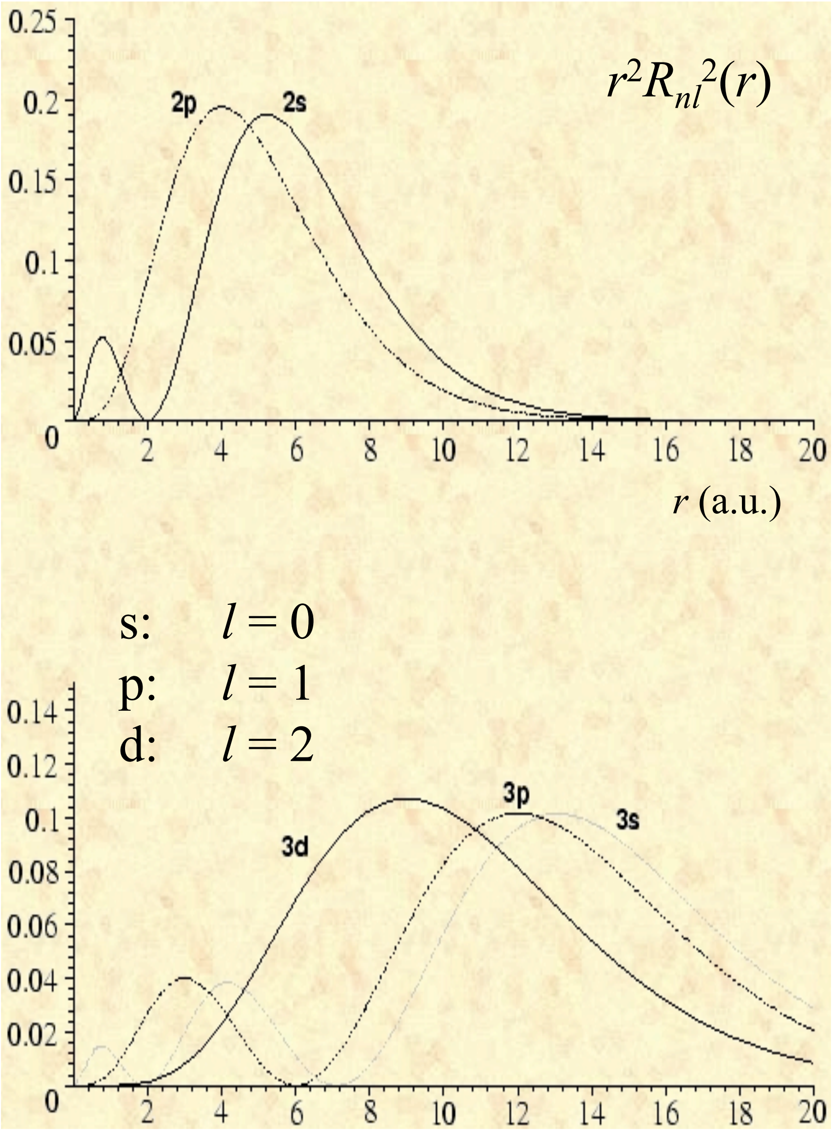


	n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$
1s	1	0	0	$2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$
2s	2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$
2p	2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
	2	1	± 1	$\left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$

⋮

Laguerre polynomial

Hydrogen Eigenstates

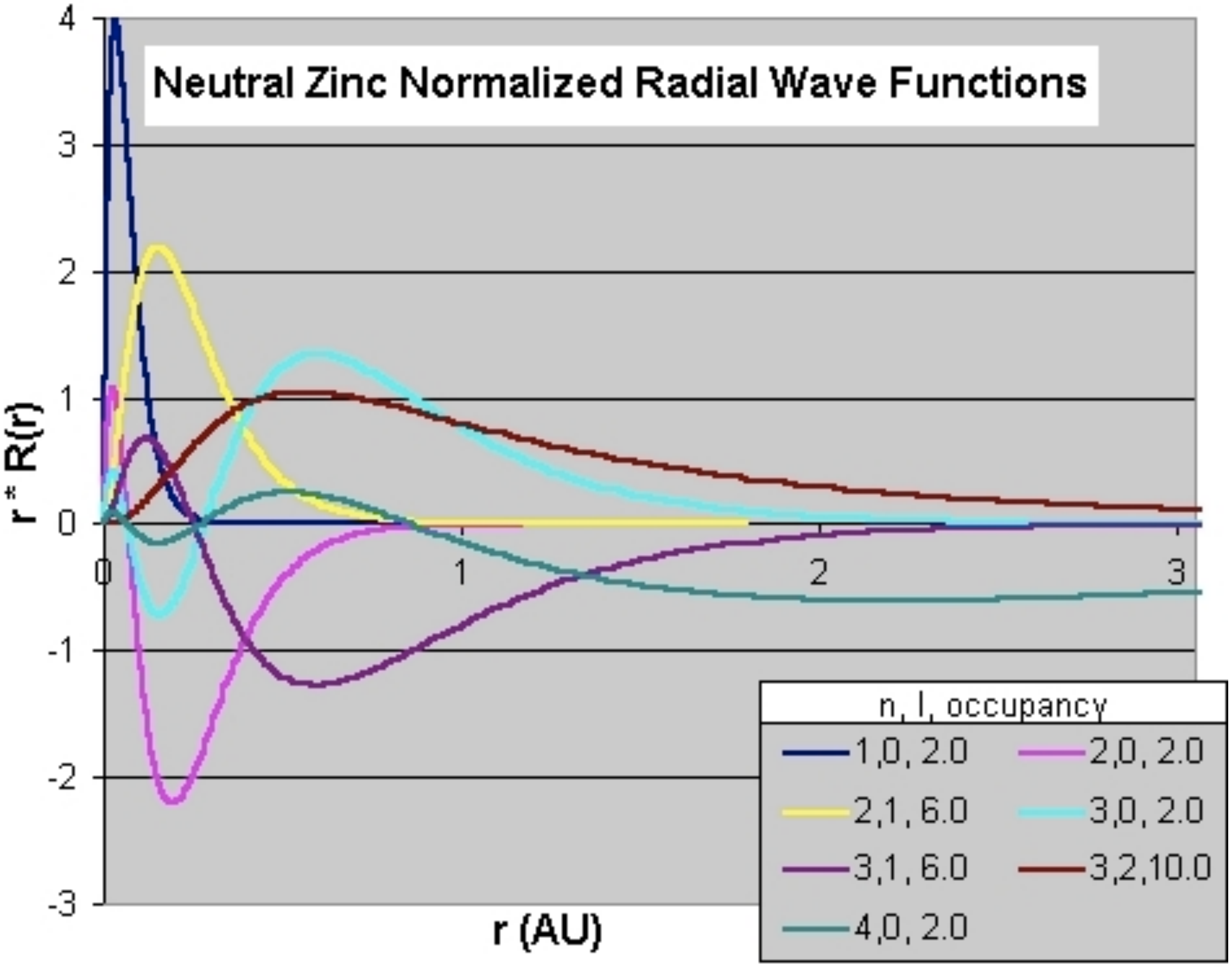


Outer shells (*i.e.*, larger *n*) spread outward

See notes on (1) Laplacian in spherical coordinates & (2) Schrodinger equation for spherically symmetric potentials

Herman-Skillman Solutions for Atoms

- **Hartree approximation ($v_{xc} = 0$) for many-electron interaction**

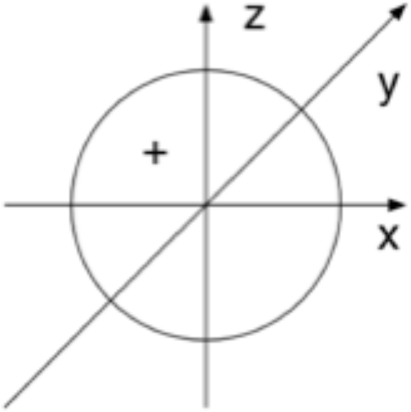


Outer shells (*i.e.*, larger *n*) still spread outward

For the inclusion of xc potential, see notes on (1) Numerical integration of radial wave function & (2) Kohn-Sham potential

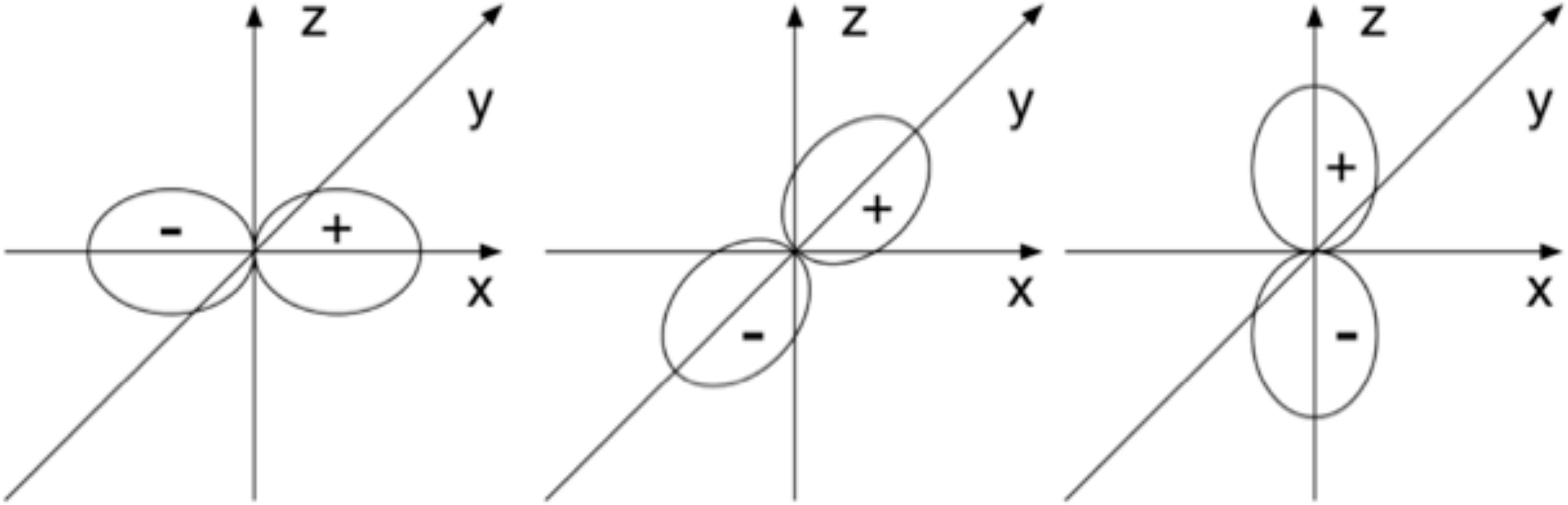
Atomic Orbitals

- **s orbital (*l* = 0)**

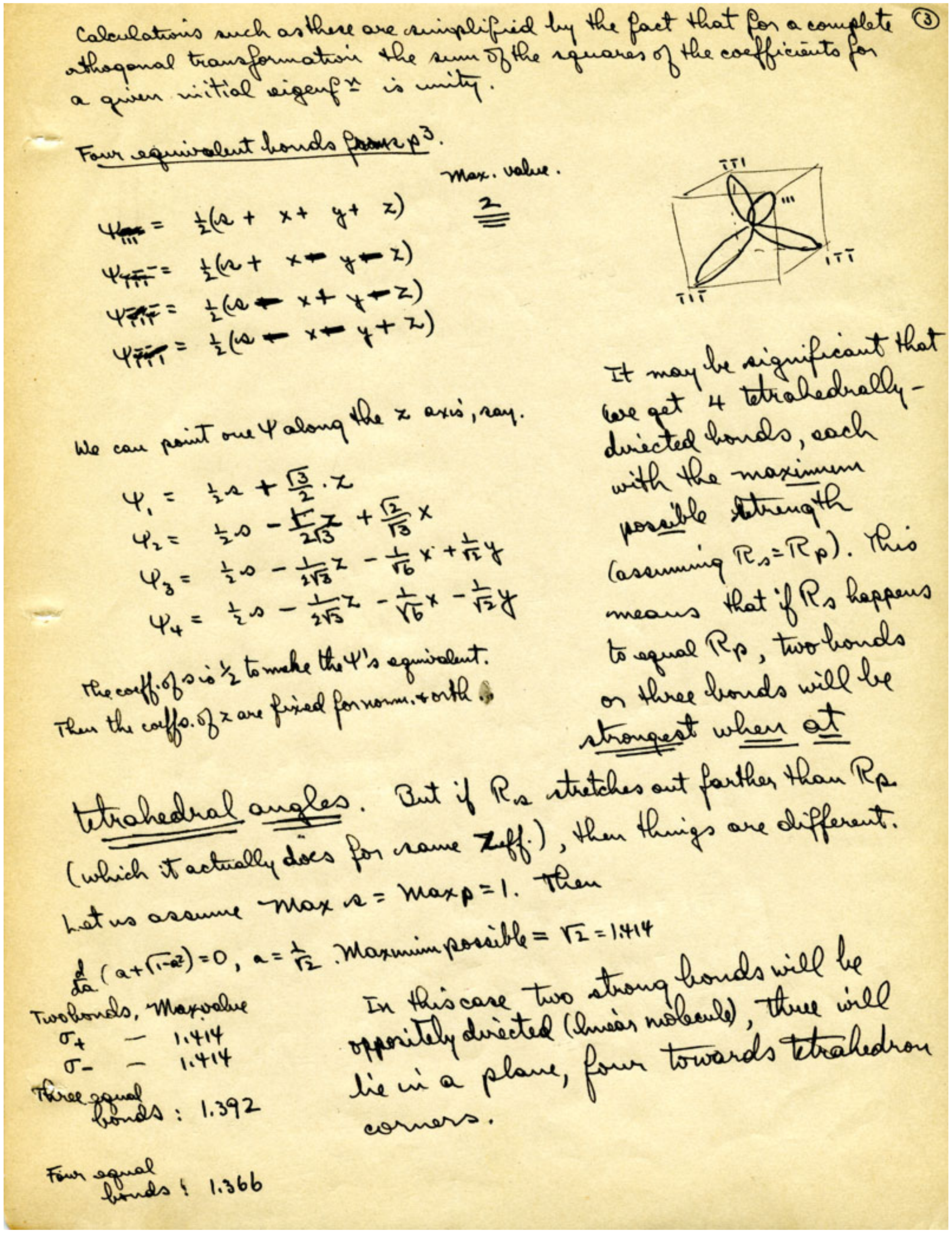


- **p orbital (*l* = 1): Cartesian representation**

$$\psi_{n1m}(r,\theta,\phi) \rightarrow \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \begin{cases} x/r \\ y/r \\ z/r \end{cases} \qquad r = \sqrt{x^2 + y^2 + z^2}$$



sp^3 Hybridization: Pauling’s Note (1930)



Calculations such as these are simplified by the fact that for a complete orthogonal transformation the sum of the squares of the coefficients for a given initial eigenf^n is unity. ③

Four equivalent bonds from sp^3.

Max. value.

$$\psi_{111} = \tfrac{1}{2}(s + x + y + z) \qquad \underline{\underline{\underline{2}}}$$

$$\psi_{1\bar{1}\bar{1}} = \tfrac{1}{2}(s + x - y - z)$$

$$\psi_{\bar{1}1\bar{1}} = \tfrac{1}{2}(s - x + y - z)$$

$$\psi_{\bar{1}\bar{1}1} = \tfrac{1}{2}(s - x - y + z)$$

We can point one ψ along the z axis, say.

$$\psi_1 = \tfrac{1}{2}s + \tfrac{\sqrt{3}}{2}\cdot z$$

$$\psi_2 = \tfrac{1}{2}s - \tfrac{1}{2\sqrt{3}}z + \tfrac{\sqrt{2}}{\sqrt{3}}x$$

$$\psi_3 = \tfrac{1}{2}s - \tfrac{1}{2\sqrt{3}}z - \tfrac{1}{\sqrt{6}}x + \tfrac{1}{\sqrt{2}}y$$

$$\psi_4 = \tfrac{1}{2}s - \tfrac{1}{2\sqrt{3}}z - \tfrac{1}{\sqrt{6}}x - \tfrac{1}{\sqrt{2}}y$$

The coeff. of s is $\tfrac{1}{2}$ to make the ψ's equivalent. Then the coeffs. of z are fixed for norm. & orth.

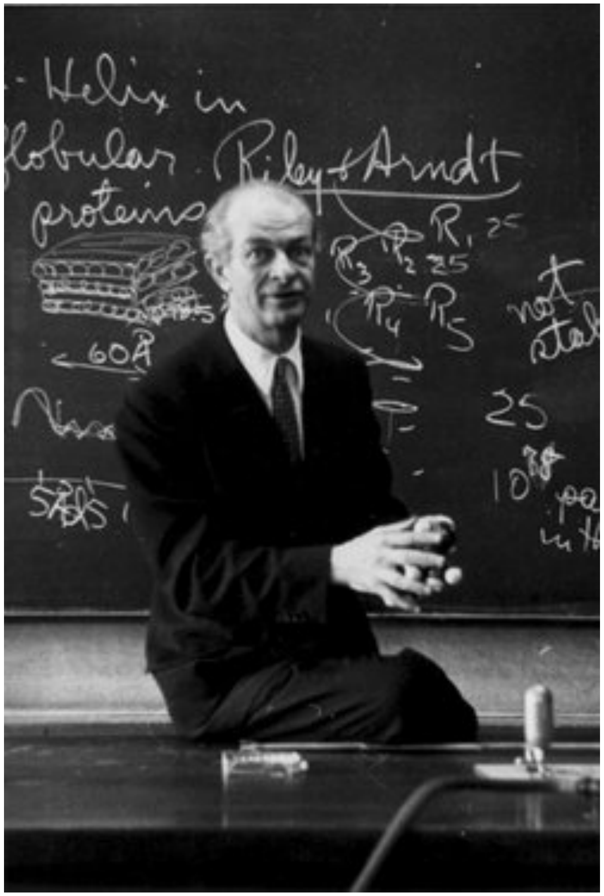
It may be significant that we get 4 tetrahedrally-directed bonds, each with the maximum possible strength (assuming $R_s = R_p$). This means that if R_s happens to equal R_p, two bonds or three bonds will be strongest when at tetrahedral angles. But if R_s stretches out farther than R_p (which it actually does for same $Z_{eff.}$), then things are different.

Let us assume max s = max p = 1. Then

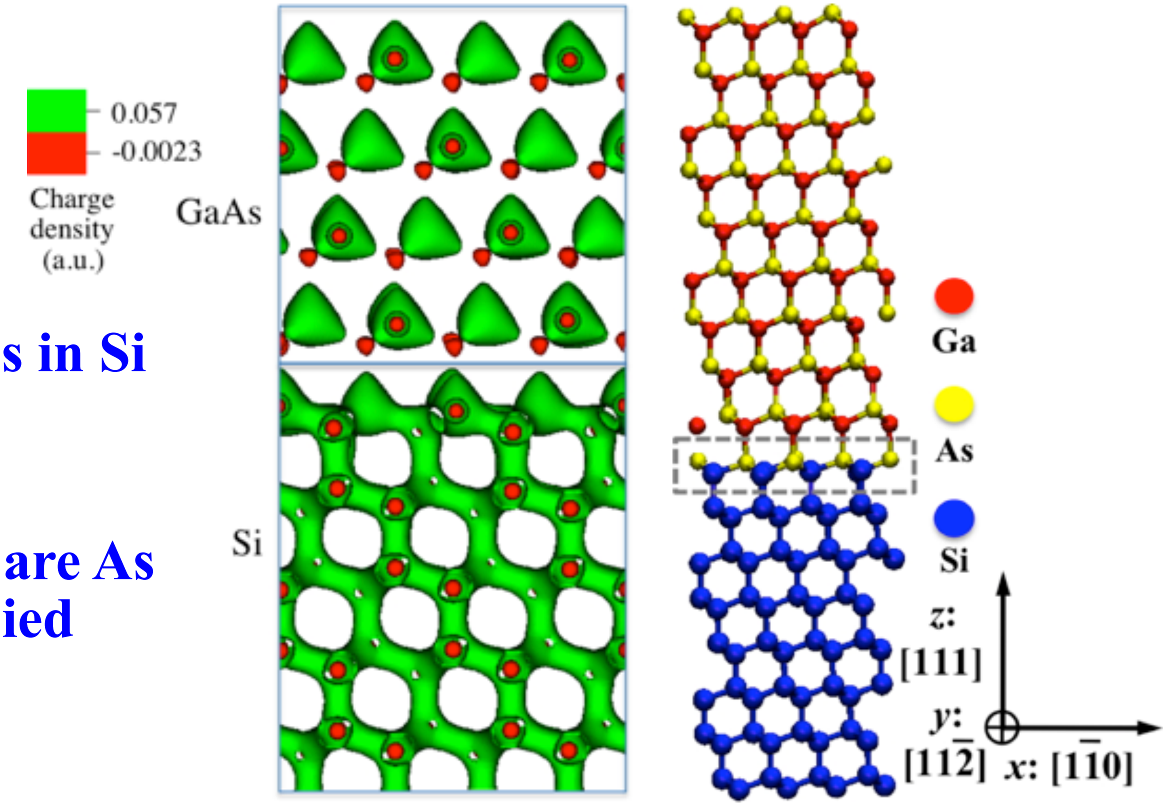
$\frac{d}{da}(a+\sqrt{1-a^2}) = 0$, $a = \frac{1}{\sqrt{2}}$. Maximum possible $= \sqrt{2} = 1.414$

Two bonds, Max. value
σ_+ — 1.414
σ_- — 1.414
Three equal bonds : 1.392
Four equal bonds : 1.366

In this case two strong bonds will be oppositely directed (linear molecule), three will lie in a plane, four towards tetrahedron corners.



Charge Density at GaAs/Si (111) Interface



- **Highest occupied states in Si have the hybrid sp^3 character**
- **Occupied GaAs states are As p-like (lowest unoccupied states are s-like)**

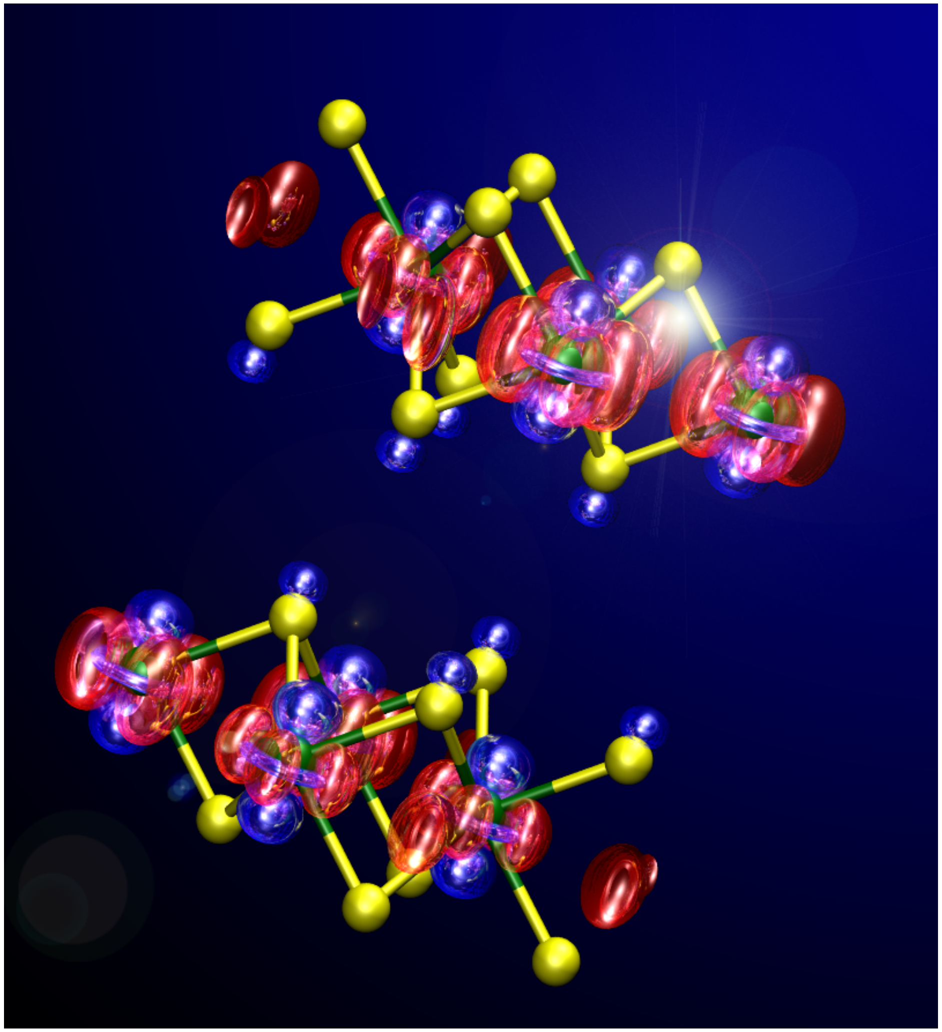
Projection of Kohn-Sham wave functions onto atomic orbitals

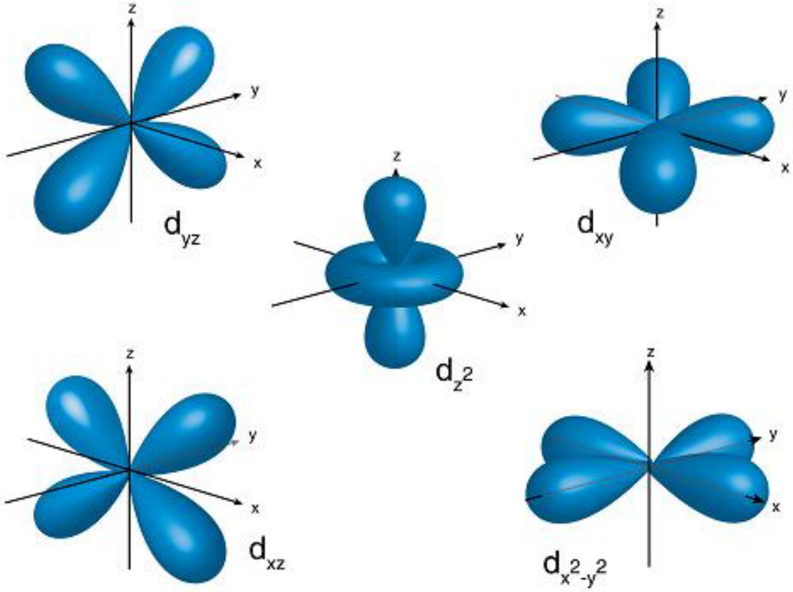
	Band	Ga 4s	Ga 4p	Ga 4d	As 4s	As 4p	As 4d	Total
	1150	0.0000	0.1157	0.0708	0.0000	0.8033	0.0101	1
	1151	0.0000	0.1158	0.0709	0.0000	0.8033	0.0100	1
Occupied	1152	0.0000	0.1166	0.0713	0.0000	**0.8017**	0.0104	1
Unoccupied	1153	**0.6763**	0.0000	0.0000	**0.3236**	0.0001	0.0000	1

Z. Yuan *et al*., *J. Appl. Phys.* **114**, 074316 ('13); *Nano Lett*. **13**, 4925 ('13)

Wave Functions in MoSe$_2$ Bilayer

- **Highest occupied states (blue) are d_{z2}-like**
- **Lowest unoccupied states (red) are d_{xy}-like**



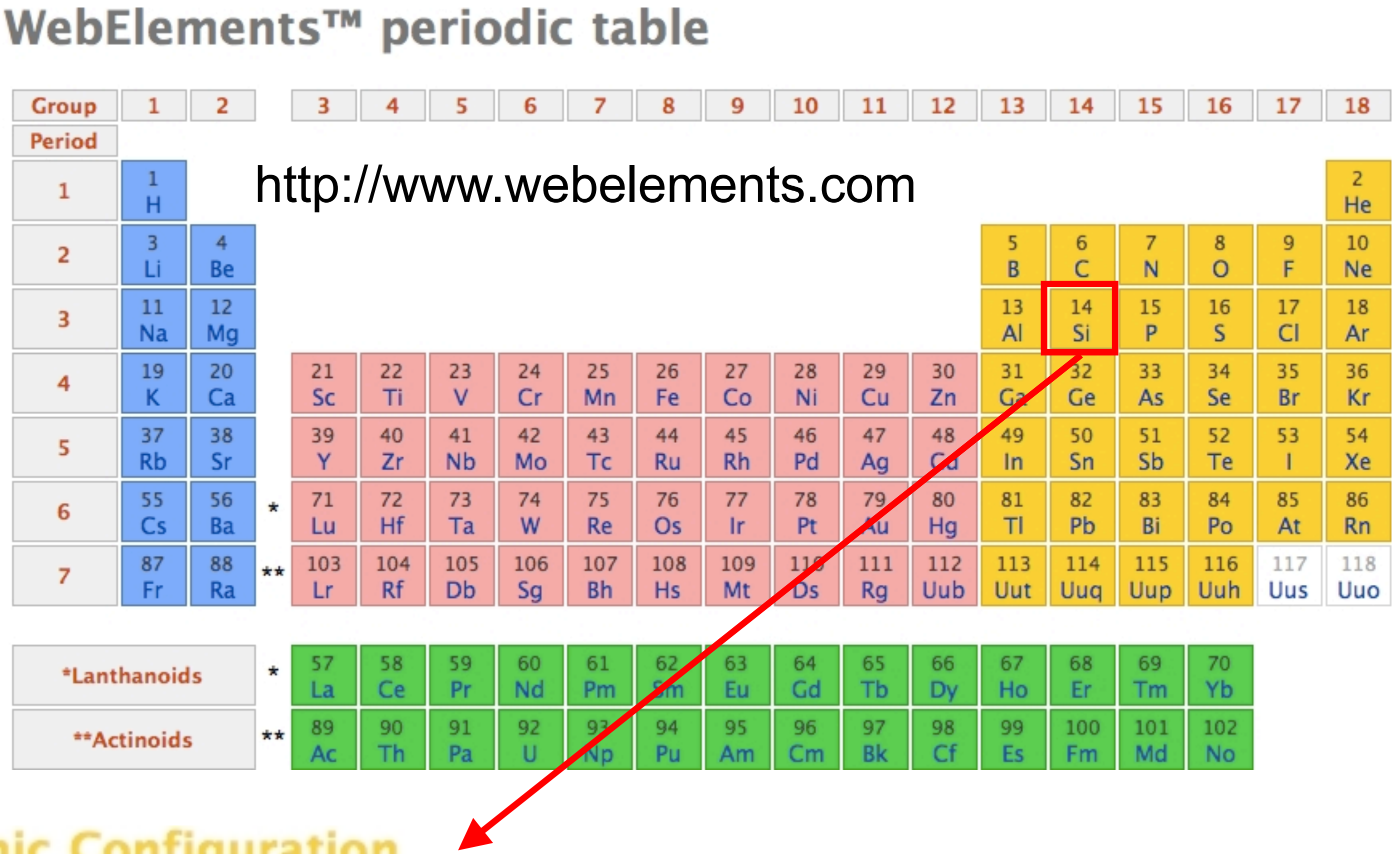


Electron
Hole

M.-F. Lin *et al*., *Nature Commun*. **8**, 1745 ('17)

Valence Electrons

- **Example: Silicon — $1s^2 2s^2 2p^6 3s^2 3p^2$**



WebElements™ periodic table

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

http://www.webelements.com

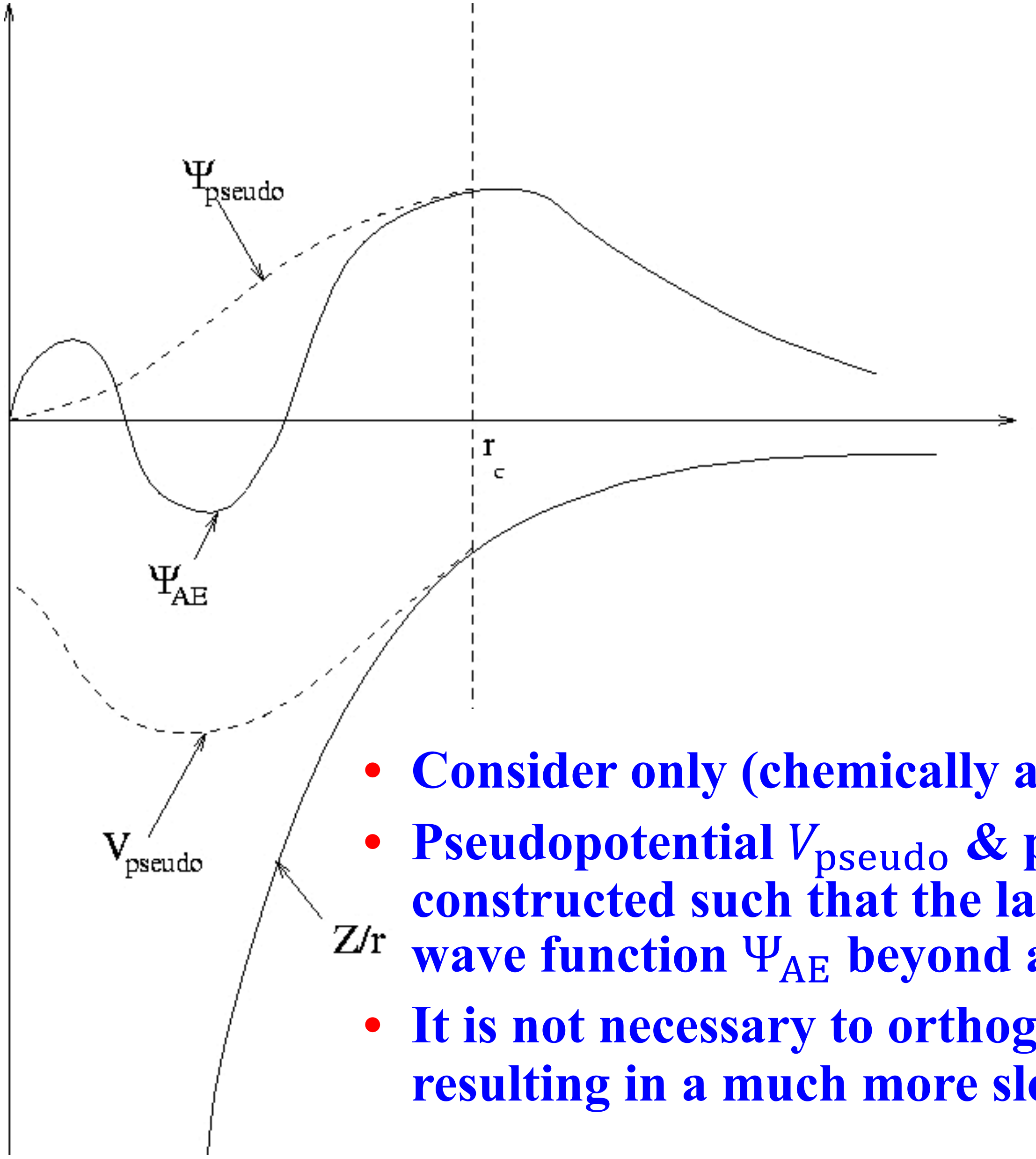
Electronic Configuration

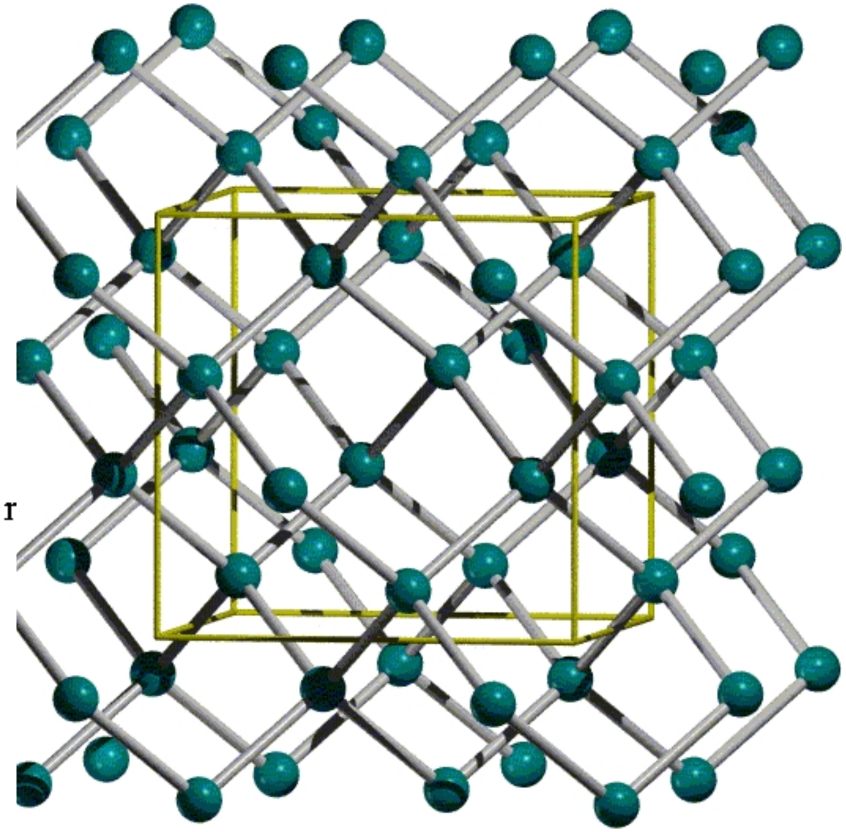
The following represents the electronic configuration and its associated term symbol for the **ground state neutral gaseous atom**. The configuration associated with silicon in its compounds is not necessarily the same.

- **Ground state electron configuration:** [Ne].$3s^2$.$3p^2$
- **Shell structure:** 2.8.4

Abstraction: Pseudopotential

- **Silicon — $1s^2 2s^2 2p^6 3s^2 3p^2$**





- **Consider only (chemically active) valence electrons**
- **Pseudopotential V_{pseudo} & pseudowave function Ψ_{pseudo} are constructed such that the latter agrees with the all-electron wave function Ψ_{AE} beyond a cutoff radius r_c**
- **It is not necessary to orthogonalize Ψ_{pseudo} to inner orbitals; resulting in a much more slowly varying function than Ψ_{AE}**

Norm-Conserving Pseudopotential

Construct pseudopotentials such that:

1. **Pseudowave functions, $R_l^{\mathrm{PP}}(r)$ $(l = 0,1,2,\dots)$, contain no nodes**
2. $R_l^{PP}(r)$ **coincides with the all-electron wave function** $R_l^{\mathrm{AE}}(r)$ **beyond a cutoff radius** r_{cl}
3. **The charge enclosed within** r_{cl} **for the AE- & pseudo-wave functions must be equal**
   $\int_0^{r_{cl}} 4\pi r^2 dr \left|R_l^{\mathrm{PP}}(r)\right|^2 = \int_0^{r_{cl}} 4\pi r^2 dr \left|R_l^{\mathrm{AE}}(r)\right|^2$
4. **AE- & pseudo-eigenenergies must be identical**
   $E_l^{\mathrm{PP}} = E_l^{\mathrm{AE}}$
5. **Conditions 2 & 4 imply: the logarithmic derivatives of the two wave functions must match at** r_{cl}
   $\left.\frac{1}{R_l^{\mathrm{PP}}(r,E_l)} \frac{dR_l^{\mathrm{PP}}(r,E_l)}{dr}\right|_{r=r_{cl}} = \left.\frac{1}{R_l^{\mathrm{AE}}(r,E_l)} \frac{dR_l^{\mathrm{AE}}(r,E_l)}{dr}\right|_{r=r_{cl}}$

Troullier & Martins, *Phys. Rev. B* **41**, 1993 ('91)

See notes on (1) Norm-conserving pseudopotential & (2) Logarithmic derivative

Local & Nonlocal Pseudopotentials

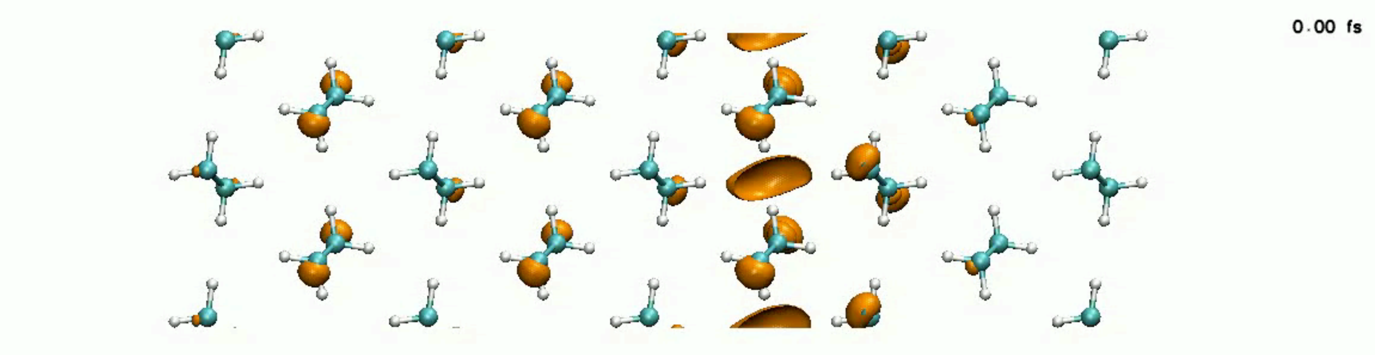
- **Ionic pseudopotential operator**

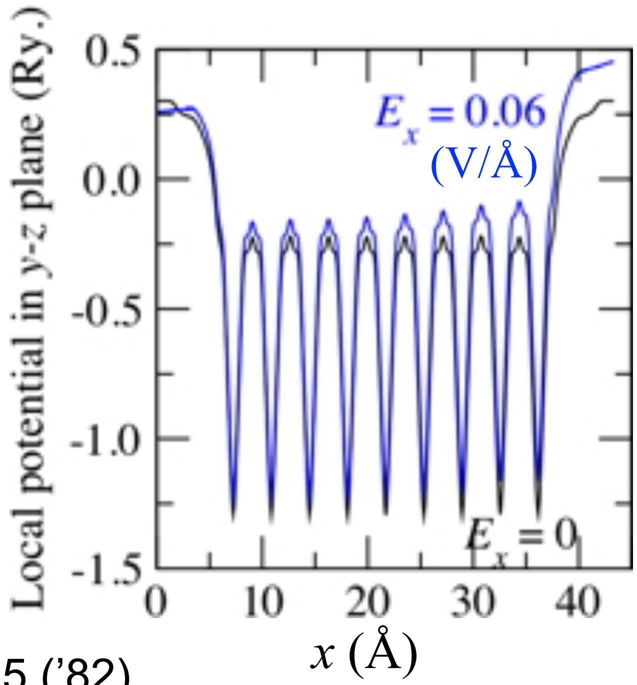
$$\hat{V}_{\text{ion}}^{\text{PP}}(r) = V_{\text{ion,local}}^{\text{PP}}(r) + \sum_{l,m} |lm\rangle \Delta V_l(r) \langle lm|$$

Common to all angular momenta

Angular-momentum dependent

- **(Example) Polyethylene slab without & with external electric field**





- **Fully nonlocal pseudopotential ~ projection**

$$\hat{V}_{\text{NL}} = \sum_{l,m} |\chi_{lm}\rangle\langle\chi_{lm}|$$

separable

Kleinman & Bylander, *Phys. Rev. Lett.* **48**, 1425 ('82)

See notes on (1) Nonlocal pseudopotential & (2) Fully nonlocal pseudopotential

Projector-Augmented Wave (PAW)

- **Core-charge correction significantly increases the transferability**

$$\tilde{v}_{\mathrm{xc}}(\mathbf{r}) = v_{\mathrm{xc}}([\rho_{\mathrm{PS}}],\mathbf{r}) + [v_{\mathrm{xc}}([\rho_{\mathrm{PS}} + \rho_{\mathrm{core}}],\mathbf{r}) - v_{\mathrm{xc}}([\rho_{\mathrm{PS}}],\mathbf{r})]$$

Louie, Froyen & Cohen, *Phys. Rev. B* **50**, 1738 ('82)

- **An "all-electron" electronic structure calculation that separates smooth pseudowave functions & rapidly varying all electron wave functions by using projection function**

detail (all electron)-out

smooth-in

$$|\Psi^{\mathrm{AE}}\rangle = |\Psi^{\mathrm{PP}}\rangle + \sum_i \left(|\phi_i^{\mathrm{AE}}\rangle - |\phi_i^{\mathrm{PP}}\rangle\right)\langle p_i|\Psi^{\mathrm{PP}}\rangle$$

Atomic partial wave

Projection function

Blochl, *Phys. Rev. B* **50**, 17953 ('94)

- **For practical construction of pseudopotentials, see** T. Sugahara *et al*., *Phys. Rep. Kumamoto Univ*. **12**, 279 ('06)