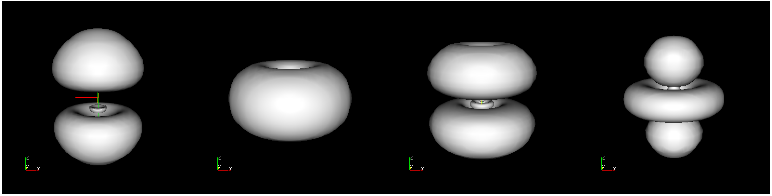
Atomic Orbitals

Atomic wavefunctions can be written as:

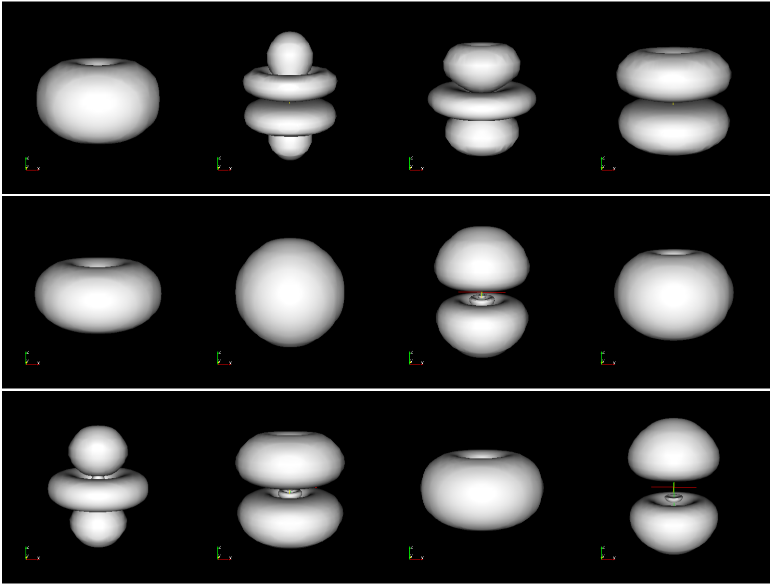
$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r) Y_{lm}(\Omega)$$

we plot $|\psi_{nlm}(\mathbf{x})|^2$ for Radium (Z=88) with electronic configuration:
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^{10} 6s^2 6p^6 7s^2$



From left to right (nlm): 610, 522, 521, 520

More Examples Atomic Orbitals



Details

We are solving the Hartree-Fock equations:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|} + \int \frac{\sum_{j=1}^{Z} |\psi_j(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|} \mathrm{d}^3 y\right) \psi_i(\mathbf{x}) +$$

$$-\sum_{j=1}^{Z} \int \frac{\psi_i(\mathbf{y})\psi_j^*(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \mathrm{d}^3 y \ \psi_j(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x})$$

(where Z is the atomic charge, $\mathbf{x}$, $\mathbf{y}$ are 3D coordinates and $\psi_i(\mathbf{x})$ are atomic orbitals) in spherical symmetry. After manipulation, they become (for closed shell atoms):

$$-\frac{1}{2} P''_{nl}(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r)\right) P_{nl}(r) +$$

$$-\sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int \frac{r_<^k}{r_>^{k+1}} P_{nl}(r') P_{n'l'}(r') \mathrm{d}r' \, P_{n'l'}(r) =$$

$$= \epsilon_{nl} P_{nl}(r)$$

Weak Formulation

$$\int_0^\infty \left(\frac{1}{2}u'(r)v'(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r)\right) u(r)v(r)\right) \mathrm{d}r +$$

$$-\sum_{n'l'} 2(2l'+1) \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(v, n'l', u, n'l') =$$

$$= \epsilon \int_0^\infty u(r)v(r)\mathrm{d}r$$

$R^k(a, b, c, d)$ is a Slater integral, $V_H(r)$ is a Hartree potential. The solution u is related to $R(r)$ from the first slide by:

$$u(r) = rR(r)$$