Excersize 1, Summer 2017

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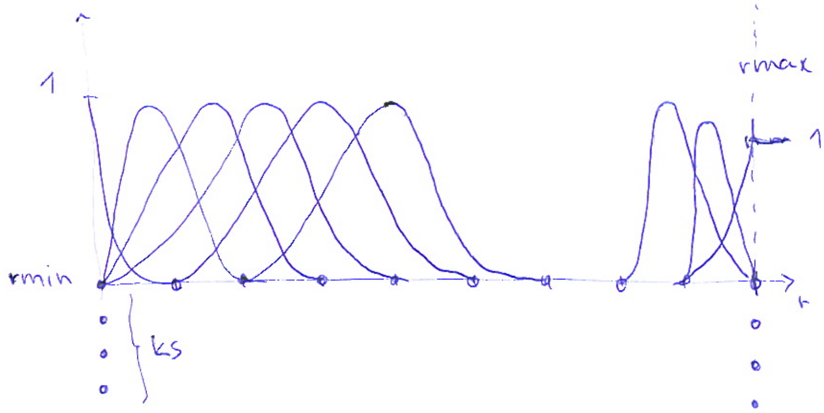
Basis set

$$\underbrace{b_{i l m}}_{\alpha}(\vec{r}) = \frac{1}{r} B_i(r)\, Y_{lm}(\hat{r})$$

- $B_i(r)$ .. B-spline - polynomial basis set
- B-spline basis of the order $ks \Rightarrow$ polynomials of the order $ks-1$
- radial grid with number of intervals nv
- Number of splines $ns = nv + k - 1$
- Each interval has ks nonzero splines $\rightarrow$ $B_i(r_e)\, B_j(r_e) = 0$ for $|i-j| \geq ks$
- knot sequence



Provided matrix elements

$$\underline{(h + J - K)\, c = S c \varepsilon}$$

$h_{\alpha\beta} = \langle b_\alpha(\vec{r}) | -\frac{1}{2}\nabla^2 - \frac{Z}{r} | b_\beta(\vec{r}) \rangle$ ... one-electron terms

function oint1($i_1, l_1, m_1, i_2, l_2, m_2, Z$)

We use the identity that transfers cartesian laplacian to spherical coordinates.

$$-\frac{1}{2}\nabla^2 \psi(\vec{r}) = \frac{1}{r}\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\hat{L}^2}{2r^2}\right](r\psi(\vec{r}))$$

$$h_{\alpha\beta} = \int_0^\infty dr\, r^2 \overbrace{\int_0^\pi d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi}^{\int d\hat{r}} \frac{1}{r} B_i(r)\, Y_{l_1 m_1}(\hat{r})\, \frac{1}{r}\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\hat{L}^2}{2r^2}\right] B_j(r)\, Y_{l_2 m_2}(\hat{r})$$

$$- Z \int_0^\infty dr \frac{B_i(r) B_j(r)}{r} \delta_{l_1 l_2} \delta_{m_1 m_2} =$$

$$= \left[\int_0^\infty dr\, B_i(r) \left(-\frac{1}{2} \frac{d^2}{dr^2} \right) B_j(r) - Z \int_0^\infty dr \frac{B_i(r) B_j(r)}{r^2} + \frac{l_1(l_1+1)}{2} \int_0^\infty dr \frac{B_i(r) B_j(r)}{r^2} \right] \delta_{l_1 l_2} \delta_{m_1 m_2}$$

Overlap terms

function ~~over1 (l_1, m_1,~~ over1($i_1, l_1, m_1, i_2, l_2, m_2$)

$$S_{\alpha\beta} = \int_0^\infty dr\, r^2 \int d^2\hat{r} \cdot \frac{1}{r^2} B_i(r) B_j(r) Y_{l_1 m_1}(\hat{r}) Y_{l_2 m_2}(\hat{r}) = \int_0^\infty dr\, B_i(r) B_j(r)\, \delta_{l_1 m_1} \delta_{l_2 m_2}$$

2-electron terms

function dint2 ($i_1, l_1, m_1, i_2, l_2, m_2, i_3, l_3, m_3, i_4, l_4, m_4$)

$$[\alpha\beta|\gamma\delta] = \int dr\, r^2 \int dr'\, r'^2 \int d^2\hat{r} \int d^2\hat{r}' \frac{1}{r^2} \frac{1}{r'^2} \frac{B_{i_1}(r) Y^*_{l_1 m_1}(\hat{r}) B_{i_2}(r) Y_{l_2 m_2}(\hat{r}) B_{i_3}(r') Y_{l_3 m_3}(\hat{r}') B_{i_4}(r') Y_{l_4 m_4}(\hat{r}')}{|\vec{r} - \vec{r}'|}$$

We separate $\vec{r}, \vec{r}'$ via: $\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{LM} \frac{r_<^L}{r_>^{L+1}} \frac{4\pi}{2L+1} Y_{LM}(\hat{r}) Y^*_{LM}(\hat{r}')$

$$[\alpha\beta|\gamma\delta] = \underbrace{\int dr \int dr' \frac{r_<^L}{r_>^{L+1}} B_{i_1}(r) B_{i_2}(r) B_{i_3}(r) B_{i_4}(r)}_{\text{radial part}} \underbrace{\sum_{LM} \underbrace{\int d\hat{r}\, Y^*_{l_1 m_1}(\hat{r}) Y_{l_2 m_2}(\hat{r}) Y_{LM}(\hat{r})}_{(-1)^{m_1} \left[\frac{(2l_1+1)(2l_2+1)(2L+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix}} \int d\hat{r}'\, Y_{l_3 m_3}(\hat{r}') Y_{l_4 m_4}(\hat{r}') Y_{LM}(\hat{r}')}_{\text{angular coupling}}$$