Closed-shell atoms

- External potential is spherically symmetric & $\left[\hat{H}, \hat{\boldsymbol{L}}\right] = 0$
- "Restricted" HF with no dependence on spin and orbital angular momentum quantum numbers works well for L=S=0 ground states of closed-shell atoms with degeneracies involving $2(2\ell+1)$
- Wave function ansatz spherical $\phi_i(\boldsymbol{r}) = \varphi_{n\ell}(r) Y_{\ell m_\ell}(\hat{\boldsymbol{r}})$
- Multiplying $\varepsilon_i \phi_i(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 \phi_i(\boldsymbol{r}) + v_H(\boldsymbol{r})\phi_i(\boldsymbol{r}) + U_{ext}(\boldsymbol{r})\phi_i(\boldsymbol{r})$ with $Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}})$

$$-\frac{1}{2}\int d\boldsymbol{r}' \, V(\boldsymbol{r}-\boldsymbol{r}') n_{HF}(\boldsymbol{r}', \boldsymbol{r}) \phi_n(\boldsymbol{r}')$$

- and integrating over $\hat{\boldsymbol{r}}$ yields equations for radial wave functions

$$\begin{aligned} \varepsilon_{n\ell}\varphi_{n\ell}(r) \quad = \quad & \int d\hat{\boldsymbol{r}} Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}}) \left\{ \left[-\frac{1}{2}\boldsymbol{\nabla}^2 - \frac{Z}{r} + v_H(\boldsymbol{r}) \right] \varphi_{n\ell}(r) Y_{\ell m_\ell}(\hat{\boldsymbol{r}}) \right. \\ & \left. -\frac{1}{2}\int d\boldsymbol{r}' \frac{n_{HF}(\boldsymbol{r}', \boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|} \varphi_{n\ell}(r') Y_{\ell m_\ell}(\hat{\boldsymbol{r}}') \right\} \end{aligned}$$

- Coulomb inserted and to be shown that rhs does not depend on m_ℓ

Check

- Note $\nabla^2\left[\varphi_{n\ell}(r)Y_{\ell m_\ell}(\hat{\boldsymbol{r}})\right] = \left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\ell(\ell+1)}{r^2}\right)\varphi_{n\ell}(r)Y_{\ell m_\ell}(\hat{\boldsymbol{r}})$
- Nuclear term also OK
- Because of full shells
$$\begin{aligned} n_{HF}(\boldsymbol{r}',\boldsymbol{r}) &= 2\sum_{n\ell}\varphi_{n\ell}(r)\varphi_{n\ell}(r')\sum_{m_\ell=-\ell}^{\ell} Y_{\ell m_\ell}(\hat{\boldsymbol{r}})Y^*_{l m_\ell}(\hat{\boldsymbol{r}}') \\ &= 2\sum_{n\ell}\varphi_{n\ell}(r)\varphi_{n\ell}(r')\frac{2\ell+1}{4\pi}P_\ell(\cos\omega) \end{aligned}$$
- So the electron density is given by
$$n^{HF}(\boldsymbol{r}) = n_{HF}(\boldsymbol{r},\boldsymbol{r}) = \frac{1}{4\pi}\sum_{n\ell}2(2\ell+1)\varphi^2_{n\ell}(r)$$
- and spherically symmetric
- So $v_H(\boldsymbol{r}) = \int d\boldsymbol{r}'\frac{n_{HF}(r')}{|\boldsymbol{r}-\boldsymbol{r}'|}$ does not depend on m_ℓ
- Use $\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} = \sum_{L=0}^{\infty}\frac{r_<^L}{r_>^{L+1}}P_L(\cos\omega)$ and $\int d\hat{\boldsymbol{r}}'\,P_L(\cos\omega) = 2\pi\int_{-1}^{+1}dx\,P_L(x) = 4\pi\delta_{L,0}$
- So Hartree potential is spherical $v_H(r) = 4\pi\int dr' r'^2\frac{n_{HF}(r')}{r_>}$

Fock term more involved

- Write
$$(\hat{v_F}\varphi_{n\ell})(r) = \frac{1}{2}\int d\hat{\boldsymbol{r}} Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}}) \int d\boldsymbol{r}' \frac{n_{HF}(\boldsymbol{r}',\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_{n\ell}(r') Y_{\ell m_\ell}(\hat{\boldsymbol{r}}')$$
$$= \frac{1}{2}\int d\hat{\boldsymbol{r}} Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}}) \int d\boldsymbol{r}' 2 \sum_{n'\ell'} \varphi_{n'\ell'}(r)\varphi_{n'\ell'}(r') \sum_{m'_\ell=-\ell'}^{\ell'} Y_{\ell' m_{\ell'}}(\hat{\boldsymbol{r}}) Y^*_{\ell' m_{\ell'}}(\hat{\boldsymbol{r}}')$$
$$\times \sum_{L=0}^{\infty}\sum_{M_L=-L}^{L} \frac{r_<^L}{r_>^{L+1}} \frac{4\pi}{2L+1} Y_{LM_L}(\hat{\boldsymbol{r}}) Y^*_{LM_L}(\hat{\boldsymbol{r}}')\varphi_{n\ell}(r') Y_{\ell m_\ell}(\hat{\boldsymbol{r}}')$$
$$= \sum_{n'\ell'} \varphi_{n'\ell'}(r) \sum_{L=0}^{\infty} \int dr' r'^2 \varphi_{n'\ell'}(r')\varphi_{n\ell}(r') \frac{r_<^L}{r_>^{L+1}} C_{\ell\ell' L}$$

- Angular integrations in
$$C_{\ell\ell' L} = \sum_{m'_\ell M_L} \frac{4\pi}{2L+1} \int d\hat{\boldsymbol{r}} Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}}) Y_{LM_L}(\hat{\boldsymbol{r}}) Y_{\ell' m'_\ell}(\hat{\boldsymbol{r}})$$
$$\int d\hat{\boldsymbol{r}}' Y^*_{\ell' m'_\ell}(\hat{\boldsymbol{r}}') Y^*_{LM_L}(\hat{\boldsymbol{r}}') Y_{\ell m_\ell}(\hat{\boldsymbol{r}}').$$

- Standard result
$$\int d\hat{\boldsymbol{r}}\, Y^*_{\ell m_\ell}(\hat{\boldsymbol{r}}) Y_{LM_L}(\hat{\boldsymbol{r}}) Y_{\ell' m'_\ell}(\hat{\boldsymbol{r}}) = \frac{\sqrt{(2\ell+1)(2\ell'+1)(2L+1)}}{\sqrt{4\pi}}$$
$$\times (-1)^{m_\ell} \begin{pmatrix} \ell & L & \ell' \\ -m_\ell & M_L & m'_\ell \end{pmatrix} \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

Further development of Fock term

- 3j-symbols in Appendix B
- Note triangles
- Use normalization $$\sum_{m'_\ell M_L} \begin{pmatrix} \ell & L & \ell' \\ -m_\ell & M_L & m'_\ell \end{pmatrix}^2 = \frac{1}{2\ell+1}$$
- to obtain

$$C_{\ell\ell' L} = (2\ell'+1) \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2$$

- also independent of m_ℓ
- Final result

$$\varepsilon_{n\ell}\varphi_{n\ell}(r) = \left\{ -\frac{1}{2}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\ell(\ell+1)}{r^2}\right] - \frac{Z}{r} + v_H(r) \right\} \varphi_{n\ell}(r) - (\hat{v}_F \varphi_{n\ell})(r)$$

- Can be solved in different ways
- One strategy discussed in Ch.10.2.3

Some properties of wave functions

- Near origin the usual behavior $\varphi_{n\ell}(r) \sim r^{\ell}$
- Asymptotic behavior more difficult due to Fock term & long-range Coulomb interaction
- It can shown that for occupied HF orbitals the asymptotic potential behaves as $\frac{N-Z-1}{r} + w(r)$ with a residual contribution that vanishes faster than $\frac{1}{r}$
- Also, all occupied orbitals decay as $\varphi_{n\ell}(r) \sim \mathrm{e}^{-\kappa r}$
- with $\kappa = \sqrt{2\varepsilon}$ determined by the last occupied HF sp energy
- For unoccupied orbits asymptotic potential less attractive and doesn't bind unoccupied states for neutral atoms