More examples

- Consider $\hat{N} = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha}$

- Determine $\left[\hat{N}, a_{\alpha_i}^{\dagger}\right] = \sum_{\alpha} \left[a_{\alpha}^{\dagger} a_{\alpha}, a_{\alpha_i}^{\dagger}\right]$

$$= a_{\alpha_i}^{\dagger}$$

- Therefore $\hat{N} \left|\alpha_1 ... \alpha_N\right\rangle = N \left|\alpha_1 ... \alpha_N\right\rangle$

Change of basis $a_{\alpha}^{\dagger} \left|0\right\rangle = \left|\alpha\right\rangle = \sum_{\lambda} \left|\lambda\right\rangle \left\langle\lambda|\alpha\right\rangle = \sum_{\lambda} a_{\lambda}^{\dagger} \left|0\right\rangle \left\langle\lambda|\alpha\right\rangle$

Can be done for any state in Fock space $\Rightarrow$ $a_{\alpha}^{\dagger} = \sum_{\lambda} \langle\lambda|\alpha\rangle a_{\lambda}^{\dagger}$

Also $a_{\alpha} = \sum_{\lambda} \langle\alpha|\lambda\rangle a_{\lambda}$

Two-body operators in Fock space

- Similar strategy $$V = \sum_{\alpha\beta}\sum_{\gamma\delta} |\alpha\beta)(\alpha\beta|V|\gamma\delta)(\gamma\delta|$$
- N-particles

$$V_N = \left\{ \begin{array}{ccccc} V(1,2)+ & V(1,3)+ & V(1,4)+ & \ldots+ & V(1,N)+ \\ & V(2,3)+ & V(2,4)+ & \ldots+ & V(2,N)+ \\ & & V(3,4)+ & \ldots+ & V(3,N)+ \\ & & & \ddots & \vdots \\ & & & & V(N-1,N) \end{array} \right.$$

$$= \sum_{i<j}^{N} V(i,j) = \frac{1}{2}\sum_{i\neq j}^{N} V(i,j)$$

- Consider

$$V(i,j)|\alpha_1..\alpha_i..\alpha_j..\alpha_N) = \sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j)|\alpha_1..\alpha_{i-1}\beta_i\alpha_{i+1}..\alpha_{j-1}\beta_j\alpha_{j+1}..\alpha_N)$$

- Matrix elements do not depend on the selected pair
- $(\beta_i\beta_j|V|\alpha_i\alpha_j)$ identical for any pair as long as quantum numbers are the same, so

$$V_N|\alpha_1\alpha_2\alpha_3...\alpha_N) = \sum_{i<j}^{N}\sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j)|\alpha_1...\beta_i...\beta_j...\alpha_N)$$

More on two-body operators

- Note: V_N symmetric and therefore commutes with antisymmetrizer
- As a consequence

$$V_N \left|\alpha_1\alpha_2\alpha_3...\alpha_N\right\rangle = \sum_{i<j}^{N} \sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j) \left|\alpha_1...\beta_i...\beta_j...\alpha_N\right\rangle$$

- Fock-space operator (proof in Phys 540)

$$\hat{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta|V|\gamma\delta) a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma$$

- accomplishes the same result for any particle number!
- Note ordering

Hamiltonian

- Most common operator $\hat{H} = \hat{T} + \hat{V}$

$$= \sum_{\alpha\beta} \langle\alpha| T |\beta\rangle \, a^\dagger_\alpha a_\beta + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta|V|\gamma\delta) a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma$$

- Notation often used $\psi^\dagger_{m_s}(\boldsymbol{r}) \equiv a^\dagger_{\boldsymbol{r}m_s}$

- Use

$$\begin{aligned}
\langle \boldsymbol{r}m_s| T |\boldsymbol{r}'m'_s\rangle &= \langle \boldsymbol{r}m_s| \frac{\boldsymbol{p}^2}{2m} |\boldsymbol{r}'m'_s\rangle \\
&= \frac{-i\hbar}{2m} \nabla \cdot \langle \boldsymbol{r}m_s| \boldsymbol{p} |\boldsymbol{r}'m'_s\rangle \\
&= \frac{-\hbar^2}{2m} \nabla^2 \langle \boldsymbol{r}m_s|\boldsymbol{r}'m'_s\rangle \\
&= \frac{-\hbar^2}{2m} \nabla^2 \delta(\boldsymbol{r}-\boldsymbol{r}')\delta_{m_s,m'_s}
\end{aligned}$$

- and

$$\begin{aligned}
(\boldsymbol{r}_1 m_{s_1} \; \boldsymbol{r}_2 m_{s_2}|V(\boldsymbol{r},\boldsymbol{r}')|\boldsymbol{r}_3 m_{s_3} \; \boldsymbol{r}_4 m_{s_4}) &= \delta(\boldsymbol{r}_1-\boldsymbol{r}_3)\delta(\boldsymbol{r}_2-\boldsymbol{r}_4) \\
&\times \; \delta_{m_{s_1},m_{s_3}} \delta_{m_{s_2},m_{s_4}} V(|\boldsymbol{r}_3-\boldsymbol{r}_4|)
\end{aligned}$$

- In this basis

$$\hat{H} = \sum_{m_s} \int d^3r \; \psi^\dagger_{m_s}(\boldsymbol{r}) \{ \frac{-\hbar^2}{2m} \nabla^2 \} \psi_{m_s}(\boldsymbol{r})$$

$$+ \frac{1}{2} \sum_{m_s m'_s} \int d^3r \int d^3r' \; \psi^\dagger_{m_s}(\boldsymbol{r}) \psi^\dagger_{m'_s}(\boldsymbol{r}') V(|\boldsymbol{r}-\boldsymbol{r}'|) \psi_{m'_s}(\boldsymbol{r}') \psi_{m_s}(\boldsymbol{r})$$

- "second quantization"

IPM for fermions in finite systems

- IPM = independent particle model
- Only consider Pauli principle
- Localized fermions
- Examples
- Hamiltonian many-body problem: $\hat{H} = \hat{T} + \hat{V} = \hat{H}_0 + \hat{H}_1$
- with $\hat{H}_0 = \hat{T} + \hat{U}$
- and $\hat{H}_1 = \hat{V} - \hat{U}$
- Suitably chosen auxiliary one-body potential U
- Many-body problem can be solved for $\hat{H}_0$!!
- Also works with fixed external potential U_{ext}

$$\hat{H} = \hat{T} + \hat{U}_{ext} + \hat{V} = \hat{H}_0 + \hat{H}_1$$

Use second quantization

- Solve $H_0 \left|\lambda\right\rangle = \varepsilon_\lambda \left|\lambda\right\rangle$

- Consider in the $\{\left|\lambda\right\rangle\}$ basis (discrete sums for simplicity)

$$\begin{aligned}\hat{H}_0 &= \sum_{\lambda\lambda'} \left\langle\lambda\right| (T+U) \left|\lambda'\right\rangle a^\dagger_\lambda a_{\lambda'} \\ &= \sum_{\lambda\lambda'} \varepsilon_{\lambda'}\ \delta_{\lambda,\lambda'}\ a^\dagger_\lambda a_{\lambda'} = \sum_\lambda \varepsilon_\lambda a^\dagger_\lambda a_\lambda\end{aligned}$$

- All many-body eigenstates of $\hat{H}_0$ are of the form

$$\left|\Phi^N_n\right\rangle = \left|\lambda_1\lambda_2 ... \lambda_N\right\rangle = a^\dagger_{\lambda_1} a^\dagger_{\lambda_2} ... a^\dagger_{\lambda_N} \left|0\right\rangle$$

- with eigenvalue

$$E^N_n = \sum_{i=1}^N \varepsilon_{\lambda_i}$$

Explicitly

- Employ $$\left[\hat{H}_0, a^\dagger_{\lambda_i}\right] = \varepsilon_{\lambda_i} a^\dagger_{\lambda_i}$$

- and therefore

$$\begin{aligned}
\hat{H}_0 \left|\lambda_1\lambda_2\lambda_3...\lambda_N\right\rangle &= \hat{H}_0 a^\dagger_{\lambda_1} a^\dagger_{\lambda_2}...a^\dagger_{\lambda_N}\left|0\right\rangle \\
&= [\hat{H}_0, a^\dagger_{\lambda_1}] a^\dagger_{\lambda_2}...a^\dagger_{\lambda_N}\left|0\right\rangle + a^\dagger_{\lambda_1}\hat{H}_0 a^\dagger_{\lambda_2}...a^\dagger_{\lambda_N}\left|0\right\rangle \\
&= [\hat{H}_0, a^\dagger_{\lambda_1}] a^\dagger_{\lambda_2}...a^\dagger_{\lambda_N}\left|0\right\rangle + a^\dagger_{\lambda_1}[\hat{H}_0, a^\dagger_{\lambda_2}]...a^\dagger_{\lambda_N}\left|0\right\rangle + ... + a^\dagger_{\lambda_1} a^\dagger_{\lambda_2}...[\hat{H}_0, a^\dagger_{\lambda_N}]\left|0\right\rangle \\
&= \left\{\sum_{i=1}^{N} \varepsilon_{\lambda_i}\right\}\left|\lambda_1\lambda_2\lambda_3...\lambda_N\right\rangle
\end{aligned}$$

- Corresponding many-body problem solved!
- Ground state $$\left|\Phi_0^N\right\rangle = \prod_{\lambda_i \le F} a^\dagger_{\lambda_i}\left|0\right\rangle$$
- Fermi sea $\Rightarrow$ F

Electrons in atoms

- Atomic units (a.u.) are standard usage
  - electron mass m_e unit of mass
  - elementary charge e unit of charge
  - length and time such that numerical values of $\hbar$ and $4\pi\epsilon_0$ are unity
  - then atomic unit of length Bohr radius

$$\text{a.u. (length)} = a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} \approx 5.29177 \times 10^{-11}\ \text{m}$$

  - and time $\text{a.u. (time)} = \dfrac{a_0}{\alpha c} \approx 2.41888 \times 10^{-17}\ \text{s}$

  - where $\alpha = \dfrac{e^2}{4\pi\epsilon_0\hbar c} \approx \dfrac{1}{137.036}$ is the fine structure constant

  - energy unit = Hartree $E_H = \dfrac{\hbar^2}{m_e a_0^2} \approx 27.2114\ \text{eV}$

Hamiltonian in a.u.

- Most of atomic physics can be understood on the basis of

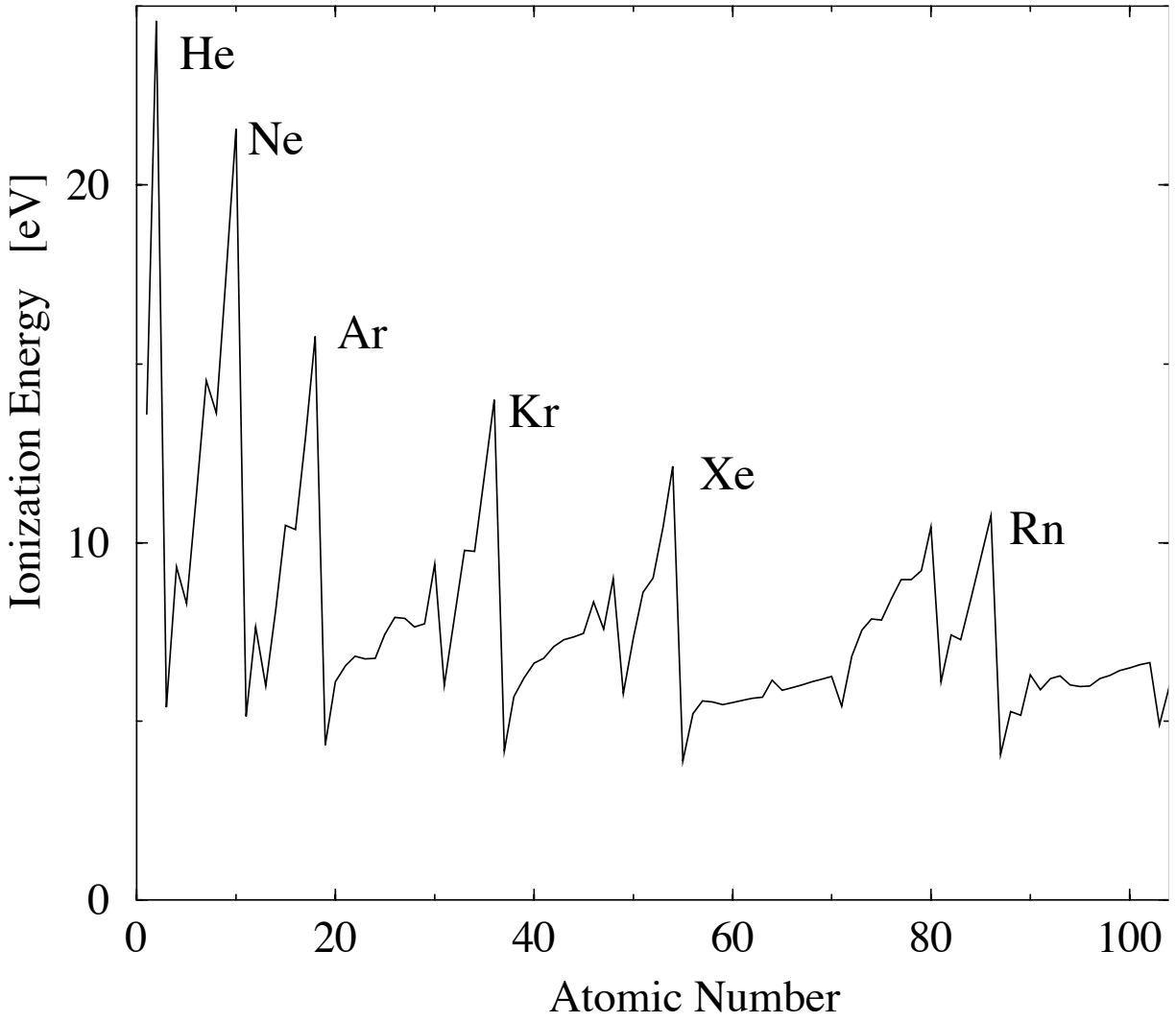
$$H_N = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2} - \sum_{i=1}^{N} \frac{Z}{|\boldsymbol{r}_i|} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + V_{mag}$$

- for most applications $V_{mag} \Rightarrow V_{so}^{eff} = \sum_i \zeta_i \, \boldsymbol{\ell}_i \cdot \boldsymbol{s}_i$

- Relativistic description required for heavier atoms
  - binding sizable fraction of electron rest mass
  - binding of lowest s state generates high-momentum components
- Sensible calculations up to Kr without V_{mag}
- Shell structure well established

Ionization energy

- Noble gases
- What does it mean?



Shell structure

- Simulate with

$$H_0^N = \sum_{i=1}^{N} H_0(i)$$

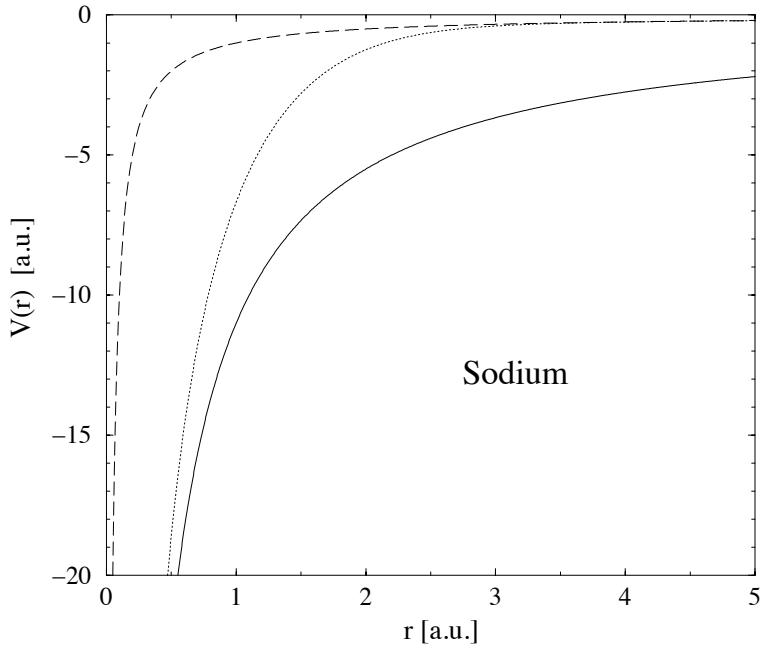
- with

$$H_0(i) = \frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{r_i} + U(\boldsymbol{r}_i)$$

- even without auxiliary potential $\Rightarrow$ shells
  - hydrogen-like: $(2\ell+1) * (2s+1)$ degeneracy
  - but $\varepsilon_n = -\frac{Z^2}{2n^2}$ does not give correct shell structure (2,10,28...
  - degeneracy must be lifted
  - how?

Other electrons

- Consider effect of electrons in closed shells for neutral Na
- large distances: nuclear charge screened to 1
- close to the nucleus: electron "sees" all 11 protons
- approximately:



- lifts H-like degeneracy: $\varepsilon_{2s} < \varepsilon_{2p}$

$$\varepsilon_{3s} < \varepsilon_{3p} < \varepsilon_{3d}$$

- "Far away" orbits: still hydrogen-like!

Ground state Na

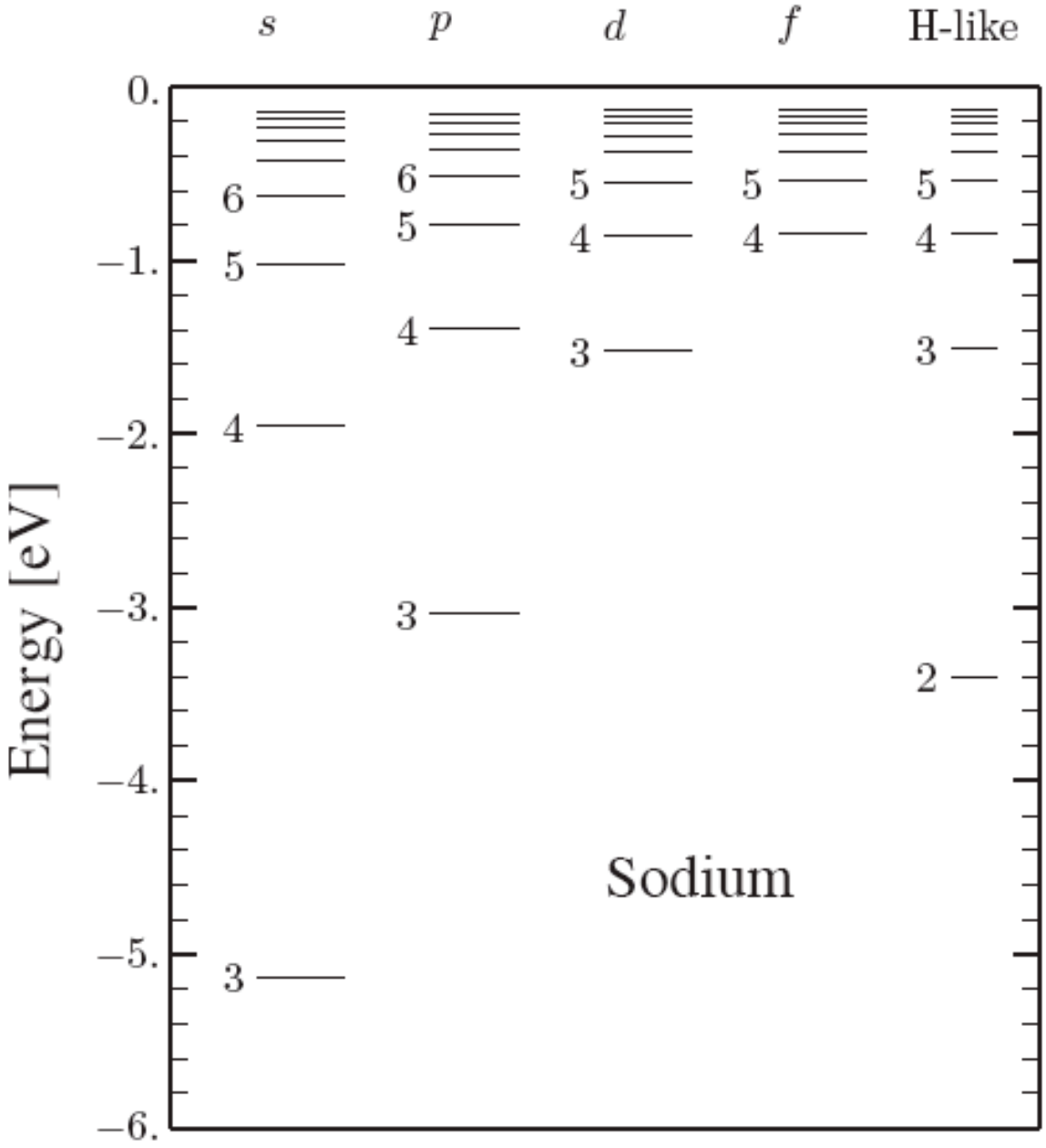
- Fill the lowest shells
- Use schematic potential

$$H_0 \left| n\ell m_\ell m_s \right\rangle = \varepsilon_{n\ell} \left| n\ell m_\ell m_s \right\rangle$$

- Ground state

$$|300 m_s, 211\tfrac{1}{2}, 211-\tfrac{1}{2}, ..., 100\tfrac{1}{2}, 100-\tfrac{1}{2}\rangle = a^\dagger_{300 m_s} a^\dagger_{211\frac{1}{2}} a^\dagger_{211-\frac{1}{2}} ... a^\dagger_{100\frac{1}{2}} a^\dagger_{100-\frac{1}{2}} |0\rangle$$

- Excited states?



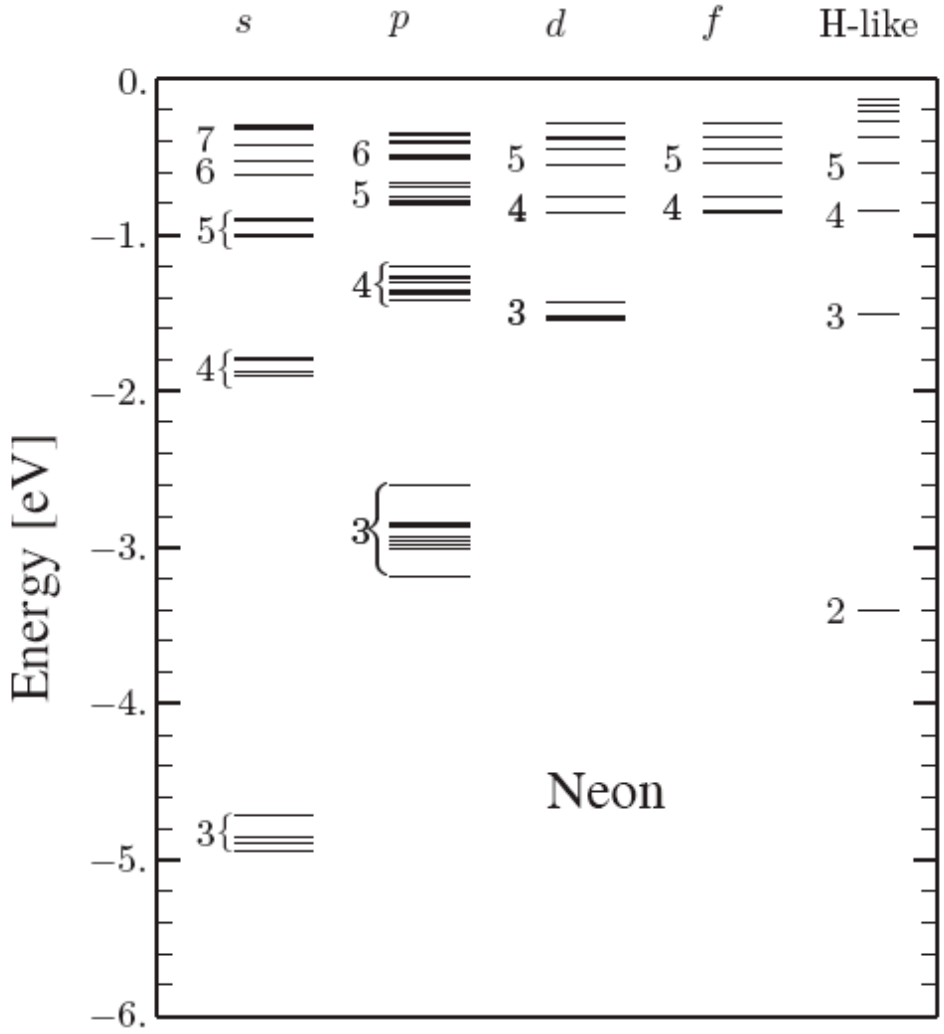
Closed-shell atoms

- Neon
- Ground state

$$|\Phi_0\rangle = a^\dagger_{211\frac{1}{2}} a^\dagger_{211-\frac{1}{2}} \ldots a^\dagger_{100\frac{1}{2}} a^\dagger_{100-\frac{1}{2}} |0\rangle$$

- Excited states

$$|n\ell\ (2p)^{-1}\rangle = a^\dagger_{n\ell} a_{2p} |\Phi_0\rangle$$



- Note the H-like states
- Splitting?
- Basic shell structure of atoms understood ⇒ IPM

Hartree-Fock

- Find Schrödinger-like equation for single-particle states that takes into account the interaction between the particles
- Replace auxiliary potential by potential calculated from interaction
- Physics: each particle moves in potential well generated by its interaction with all the other particles in the system
- In turn: these particles must move in the same potential well --> democratic --> self-consistent problem
- Several derivations:
  - Variational: Slater determinant that minimizes the energy
  - Propagator equation that includes lowest-order effect in interaction
  - Here: heuristic

Development

- Consider following expectation values in a general basis

$$\begin{aligned}
\langle \alpha_1 ... \alpha_N | \hat{T} | \alpha_1 ... \alpha_N \rangle &= \sum_{\alpha\beta} \langle \alpha | T | \beta \rangle \langle \alpha_1 ... \alpha_N | a_\alpha^\dagger a_\beta | \alpha_1 ... \alpha_N \rangle \\
&= \sum_{\alpha,\beta \in \{\alpha_i\}} \langle \alpha | T | \beta \rangle \langle \alpha_1 ... \alpha_N | \left(\delta_{\alpha\beta} - a_\beta a_\alpha^\dagger \right) | \alpha_1 ... \alpha_N \rangle \\
&= \sum_{i=1}^{N} \langle \alpha_i | T | \alpha_i \rangle
\end{aligned}$$

$$\begin{aligned}
\langle \alpha_1 ... \alpha_N | \hat{V} | \alpha_1 ... \alpha_N \rangle &= \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta|V|\gamma\delta) \langle \alpha_1 ... \alpha_N | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | \alpha_1 ... \alpha_N \rangle \\
&= \frac{1}{2} \sum_{\alpha\beta\gamma\delta \in \{\alpha_i\}} (\alpha\beta|V|\gamma\delta) \langle \alpha_1 ... \alpha_N | \left(\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma} \right) | \alpha_1 ... \alpha_N \rangle \\
&= \frac{1}{2} \sum_{\alpha\beta \in \{\alpha_i\}} [(\alpha\beta|V|\alpha\beta) - (\alpha\beta|V|\beta\alpha)]
\end{aligned}$$

Development

- Consider 1 particle explicitly with the other in their HF orbits

$$\begin{aligned}
\langle \mu\alpha_2...\alpha_N | \hat{T} | \nu\alpha_2...\alpha_N \rangle &= \sum_{\alpha\beta} \langle \alpha | T | \beta \rangle \langle \mu\alpha_2...\alpha_N | a_\alpha^\dagger a_\beta | \nu\alpha_2...\alpha_N \rangle \\
&= \sum_{\alpha\in\{\alpha_i\mu\}\beta\in\{\alpha_i\nu\}} \langle \alpha | T | \beta \rangle \langle \alpha_2...\alpha_N | a_\mu a_\alpha^\dagger a_\beta a_\nu^\dagger | \alpha_2...\alpha_N \rangle \\
&= \sum_{\alpha\in\{\alpha_i\mu\}\beta\in\{\alpha_i\nu\}} \langle \alpha | T | \beta \rangle \langle \alpha_2...\alpha_N | \left(\delta_{\alpha\mu} - a_\alpha^\dagger a_\mu\right)\left(\delta_{\beta\nu} - a_\nu^\dagger a_\beta\right) | \alpha_2...\alpha_N \rangle \\
&= \langle \mu | T | \nu \rangle + \delta_{\mu\nu} \langle \alpha_2...\alpha_N | \hat{T} | \alpha_2...\alpha_N \rangle
\end{aligned}$$

- Same procedure

$$\langle \mu\alpha_2...\alpha_N | \hat{V} | \nu\alpha_2...\alpha_N \rangle = \sum_{\alpha\in\{\alpha_i\}} [(\mu\alpha|V|\nu\alpha) - (\mu\alpha|V|\alpha\nu)] + \delta_{\mu\nu} \langle \alpha_2...\alpha_N | \hat{V} | \alpha_2...\alpha_N \rangle$$

- Interpret as average interaction energy

$$\langle \mu | U_{HF} | \nu \rangle = \sum_{\alpha\in\{\alpha_i\}} [(\mu\alpha|V|\nu\alpha) - (\mu\alpha|V|\alpha\nu)] \equiv \sum_{\alpha\in\alpha_i} \langle \mu\alpha | V | \nu\alpha \rangle$$

- Solve one-body problem with $\left(T + U_{HF}\right) | \alpha_i \rangle = \varepsilon_i | \alpha_i \rangle$
- What is the problem with this?

Further development

- Requires self-consistency procedure
- Start with guess (problem set for bound states) --> $\{|\alpha_i^{(0)}\rangle\}$

$$\langle \alpha_i^{(0)}| \, U_{HF}^{(0)} \, |\alpha_j^{(0)}\rangle = \sum_k \langle \alpha_i^{(0)} \alpha_k^{(0)}| \, V \, |\alpha_j^{(0)} \alpha_k^{(0)}\rangle$$

- Solve

$$\left(T + U_{HF}^{(0)}\right) |\alpha_m^{(1)}\rangle = \varepsilon_m^{(1)} \, |\alpha_m^{(1)}\rangle$$

$$\sum_j \left\{ \langle \alpha_i^{(0)}| \, T + U_{HF}^{(0)} \, |\alpha_j^{(0)}\rangle \right\} \langle \alpha_j^{(0)} | \alpha_m^{(1)}\rangle = \varepsilon_m^{(1)} \langle \alpha_i^{(0)} | \alpha_m^{(1)}\rangle$$

- Then

$$\langle \alpha_i^{(1)}| \, U_{HF}^{(1)} \, |\alpha_j^{(1)}\rangle = \sum_k \langle \alpha_i^{(1)} \alpha_k^{(1)}| \, V \, |\alpha_j^{(1)} \alpha_k^{(1)}\rangle$$

- Again

$$\left(T + U_{HF}^{(1)}\right) |\alpha_m^{(2)}\rangle = \varepsilon_m^{(2)} \, |\alpha_m^{(2)}\rangle$$

$$\sum_j \left\{ \langle \alpha_i^{(1)}| \, T + U_{HF}^{(1)} \, |\alpha_j^{(1)}\rangle \right\} \langle \alpha_j^{(1)} | \alpha_m^{(2)}\rangle = \varepsilon_m^{(2)} \langle \alpha_i^{(1)} | \alpha_m^{(2)}\rangle$$

- and so on until self-consistent!

- Solution in coordinate space...

Ingredients

- Interaction term

$$\begin{aligned}\langle \boldsymbol{r} m_s | \, U_{HF} \, | \boldsymbol{r}' m_s' \rangle &= \sum_k \langle \boldsymbol{r} m_s \alpha_k | \, V \, | \boldsymbol{r}' m_s' \alpha_k \rangle \\ &= \sum_k \int d^3 r_1 \int d^3 r_2 \sum_{m_1 m_2} \langle \alpha_k | \boldsymbol{r}_1 m_1 \rangle \, \langle \boldsymbol{r} m_s \boldsymbol{r}_1 m_1 | \, V \, | \boldsymbol{r}' m_s' \boldsymbol{r}_2 m_2 \rangle \, \langle \boldsymbol{r}_2 m_2 | \alpha_k \rangle\end{aligned}$$

- Interaction

$$(\boldsymbol{r}_1 m_{s_1}, \boldsymbol{r}_2 m_{s_2} | \, V \, | \boldsymbol{r}_3 m_{s_3}, \boldsymbol{r}_4 m_{s_4}) = \delta_{m_{s1}, m_{s3}} \delta_{m_{s2}, m_{s4}} \delta(\boldsymbol{r}_1 - \boldsymbol{r}_3) \delta(\boldsymbol{r}_2 - \boldsymbol{r}_4) V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$$

- Direct term

$$\langle \boldsymbol{r} m_s | \, U_{HF}^D \, | \boldsymbol{r}' m_s' \rangle = \delta(\boldsymbol{r} - \boldsymbol{r}') \delta_{m_s m_s'} \sum_k \int d^3 r_1 \sum_{m_1} V(\boldsymbol{r} - \boldsymbol{r}_1) |\langle \boldsymbol{r}_1 m_1 | \alpha_k \rangle|^2$$

- Exchange

$$\begin{aligned}\langle \boldsymbol{r} m_s | \, U_{HF}^E \, | \boldsymbol{r}' m_s' \rangle &= -\sum_k (\boldsymbol{r} m_s \alpha_k | V | \alpha_k \boldsymbol{r}' m_s') \\ &= -\sum_k \int d^3 r_1 \int d^3 r_2 \sum_{m_1 m_2} \langle \alpha_k | \boldsymbol{r}_1 m_1 \rangle (\boldsymbol{r} m_s \boldsymbol{r}_1 m_1 | V | \boldsymbol{r}_2 m_2 \boldsymbol{r}' m_s') \langle \boldsymbol{r}_2 m_2 | \alpha_k \rangle \\ &= -\sum_k \langle \alpha_k | \boldsymbol{r}' m_s' \rangle V(\boldsymbol{r} - \boldsymbol{r}') \langle \boldsymbol{r} m_s | \alpha_k \rangle\end{aligned}$$

- Nonlocal potential

More and including external field

- Notation for HF wave function $\langle \boldsymbol{r} m_s | \alpha_k \rangle = \phi_k(\boldsymbol{r}, m_s)$
- Remember $(T + U_{ext} + U_{HF}) |\alpha_k\rangle = \varepsilon_k |\alpha_k\rangle$
- becomes

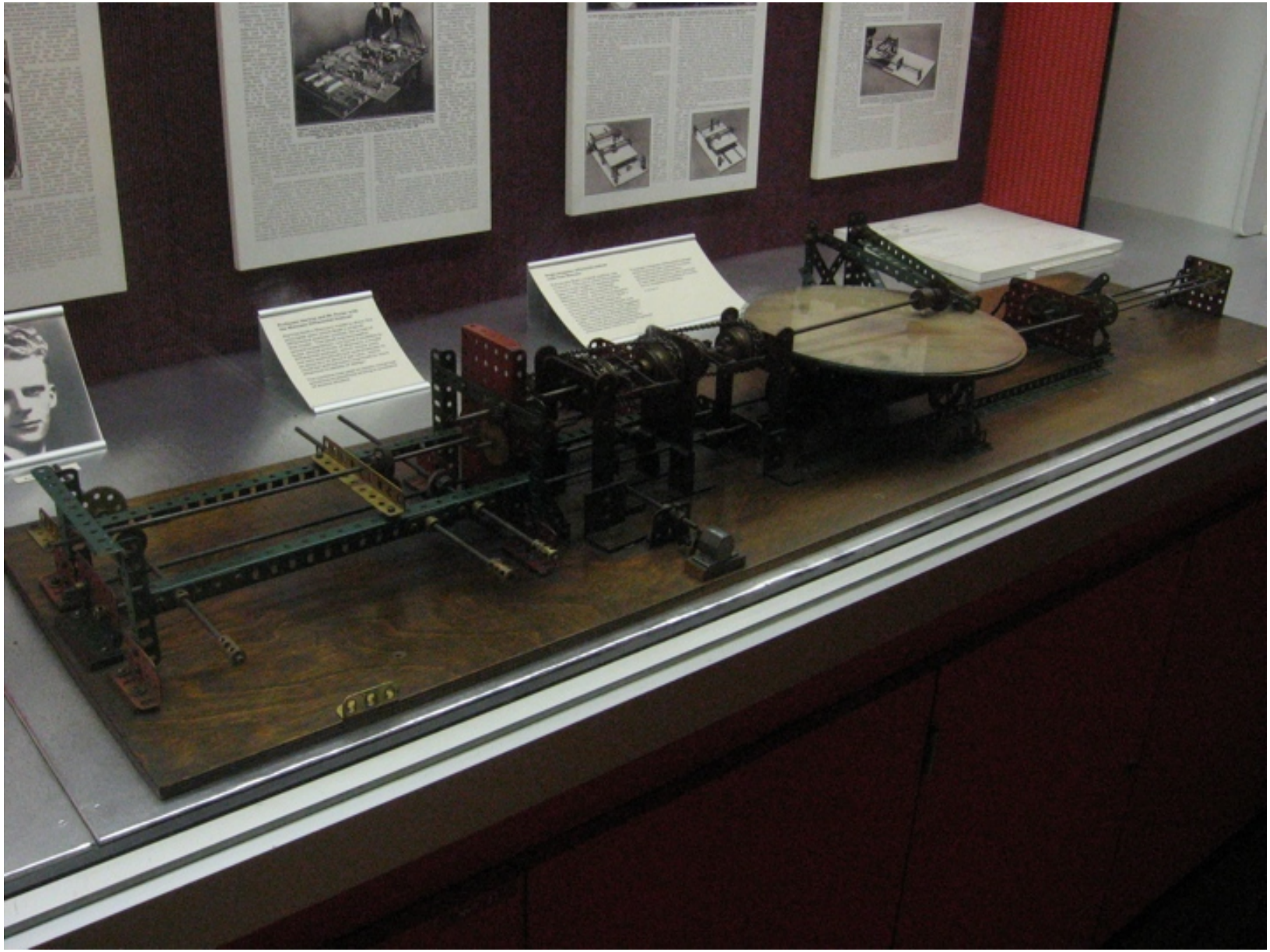
$$\varepsilon_k \phi_k(\boldsymbol{r}, m_s) = -\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \phi_k(\boldsymbol{r}, m_s) + U_{ext}(\boldsymbol{r}) \phi_k(\boldsymbol{r}, m_s)$$
$$+ \left[\int d\boldsymbol{r}' V(\boldsymbol{r} - \boldsymbol{r}') \sum_{m_s'} n^{HF}(\boldsymbol{r}' m_s', \boldsymbol{r}' m_s') \right] \phi_k(\boldsymbol{r}, m_s)$$
$$- \sum_{m_s'} \int d\boldsymbol{r}' V(\boldsymbol{r} - \boldsymbol{r}') n^{HF}(\boldsymbol{r}' m_s', \boldsymbol{r} m_s) \phi_k(\boldsymbol{r}', m_s')$$

- with

$$n^{HF}(\boldsymbol{r}' m_s', \boldsymbol{r} m_s) = \sum_{n=1}^{N} \phi_n(\boldsymbol{r}, m_s) \phi_n^*(\boldsymbol{r}', m_s')$$

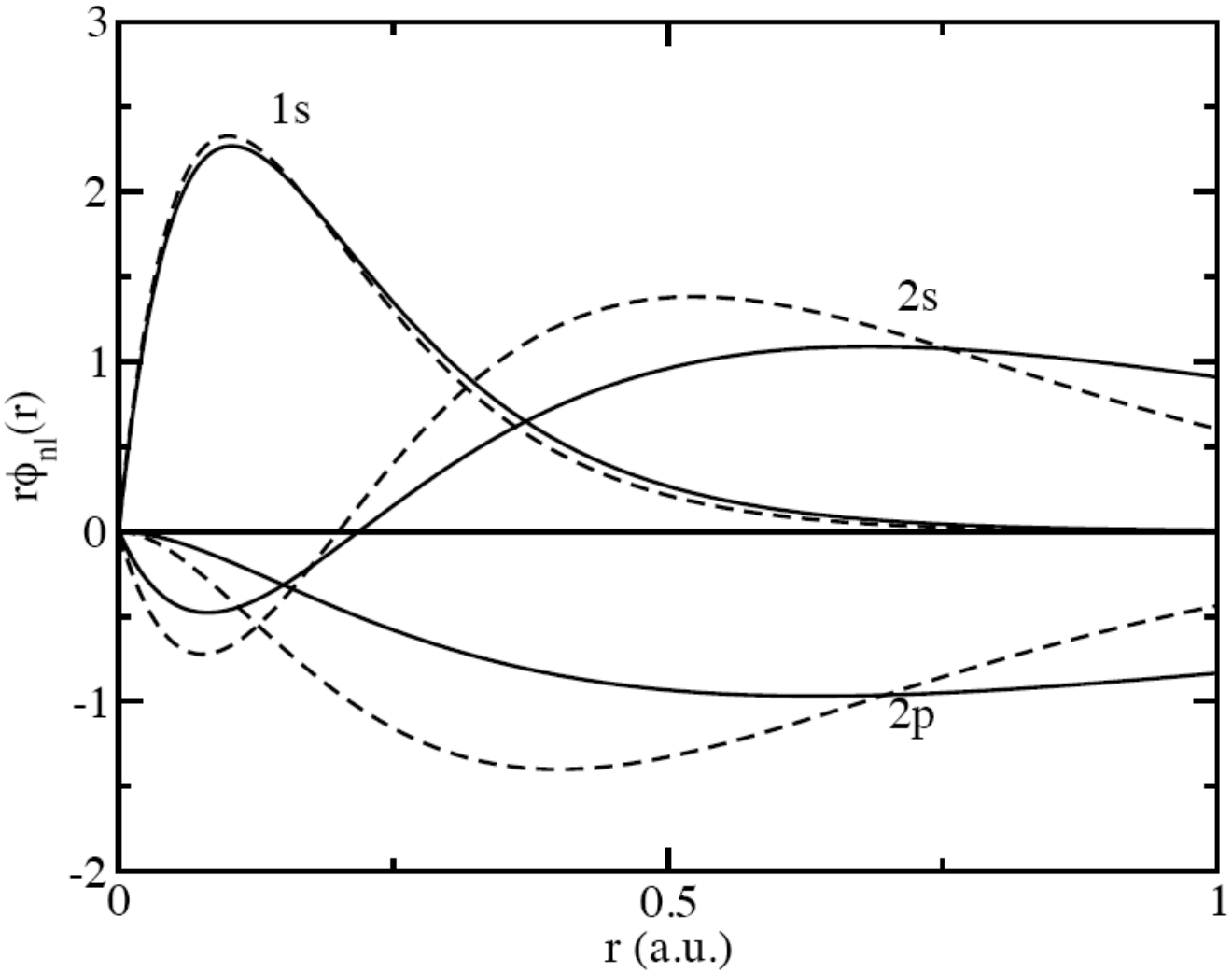
- Exchange term of interaction --> Fock term
- Direct term: Hartree
- Only Hartree --> Pauli principle correction

Douglas Hartree



Wave functions

- Ne wave functions (solid lines)
- compared with hydrogenic wave functions (dashed lines)



Comparison with experimental data

- L=S=0 closed-shell atoms (a.u. energy: Hartree = 27.2113845 eV)
- Be and Mg not pure closed shells
- Need much better results to do chemistry! (mH)

		Removal energies		Total energy	
		HF	Exp.	HF	Exp.
He	$1s$	-0.918	-0.9040	-2.862	-2.904
Be	$1s$	-4.733	-4.100	-14.573	-14.667
	$2s$	-0.309	-0.343		
Ne	$1s$	-32.77	-31.70	-128.547	-128.928
	$2s$	-1.930	-1.782		
	$2p$	-0.850	-0.793		
Mg	$1s$	-49.03	-47.91	-199.615	-200.043
	$2s$	-3.768	-3.26		
	$2p$	-2.283	-1.81		
	$3s$	-0.253	-0.2811		
Ar	$1s$	-118.6	-117.87	-526.818	-527.549
	$2s$	-12.32	-12.00		
	$2p$	-9.571	-9.160		
	$3s$	-1.277	-1.075		
	$3p$	-0.591	-0.579		