ELECTRON CORRELATION

He:

(via coulomb interaction)

Coulomb correlation

Electrons "avoid" each other
Their motion is "correlated"

The most preferable positions of two electrons

This effect is not described by any theoretical model
Defined within the single configuration approximation

Fermi corr. ⇒
(only correlation between electrons with the same projections
of spin is included due to the properties of Slater determin.)

"Correlation energy"
Non-relativistic energy, the best for the
Non-relativistic Hamiltonian

\[ H = \sum_i h(i) + \sum_{i<j} \frac{1}{r_{ij}} \]

\[ E_{\text{exp}} - E_{\text{rel}} = E_{\text{rel}} \]

Error of SCF

\[ E_{\text{corr}} = E_{\text{rel}} - E_{\text{HF}} \]

Rather estimated than evaluated
\( < 1\% \) of \( E_{\text{total}} \)

Hartree-Fock limit:
Energy obtained from the
Model based on single conf.
Approximation, defined in the
Terms of single particle
Approximation

Various approximations

\[ \text{E}^{\text{SCF}} \text{ in algebraic approximation}
\quad \text{(limited basis set and extended)} \]

Close to the Hartree-Fock limit (practice)
\[ \text{E}_{\text{HF}} - \text{Hartree-Fock limit (complete basis set)} \]

"Full CI"
\[ E_{\text{rel}} \]

Common practice
\[ E_{\text{exp}} \]

"Experimental" correlation energy
HOW TO IMPROVE THE RESULTS OF SCF?

CORRELATION FACTORS \{ \text{INTRODUCE THE DISTANCE } r_{12} \}
CORRELATED FUNCTIONS \text{\textsc{\textsc{EXPLICITE INTO FUNCTION}}}

He

$$
\Psi = \psi(1)\psi(2)(1 + c r_{12})
$$

VARIATIONAL PARAMETER

FOR GREATER $r_{12} \Rightarrow$ GREATER VALUES OF $\Psi \Rightarrow$ GREATER $|\Psi|^2 \Rightarrow$

BETTER DESCRIPTION OF ELECTRON CORRELATION

MORE ADVANCED

$$(1 + c_1 r_1 + c_2 r_2 + c_3 r_{12}^s)$$

$c_1, c_2, c_3$ - LINEAR VARIATIONAL PARAMETERS

$p, q, s$ - VARIATIONAL PARAMETERS

1959 - C.J. Pekeris: 1027 PARAMETERS $\Rightarrow$ ENERGY OF HE WITHIN
THE ACCURACY OF 7 DIGITS, WITHIN THE ERROR OF EXPERIMENT ($\sim 0.1 \text{cm}^{-1}$).

THE SOLUTION OF NON-RELATIVISTIC EIGENVALUE PROBLEM FOR HE
IS KNOWN WITH THE ACCURACY OF 14 DIGITS.

HOW TO IMPROVE THE RESULTS OF SCF FOR $N > 2$
ELECTRON SYSTEMS?

MÖLLER-PLESSET PERTURBATION THEORY

$$
H = \sum_i h(i) + \sum_{i<j} \frac{e^2}{r_{ij}} \quad H\psi = E\psi
$$

$$
\sum_i F(i) = \sum_i h(i) + \sum_{q} (2 j_q(i) - K_q(i)) \quad F(i)\psi_i = E_i\psi_i
$$

$$
H = \sum_i F(i) + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i \sum_q (2 j_q(i) - K_q(i))
$$

BEYOND $H-F$ \text{\textsc{\textsc{NON-CENTRAL PART OF COULOMB INT.}}}
\text{\textsc{\textsc{RESponsible FOR ELECTRON CORREL.}}
\[ H = \sum_i F(i) + \sum_{i \neq j} \frac{e^2}{\epsilon_{ij}} - \sum_i \sum_q (2J_q(i) - K_q(i)) \]

\[ H = H_0 + \lambda V \]

\[ E^0 = \langle \psi^0 | H_0 | \psi^0 \rangle = \langle \psi^0 | \sum_i F(i) | \psi^0 \rangle = \sum_i \varepsilon_i \quad (= \sum \varepsilon_p) \]

\[ E^{(1)} = \langle \psi^0 | V_1 | \psi^0 \rangle = \psi^0 \approx \psi_{HF} \]

\[ E_{HF} = 2 \sum_{p=1}^{N/2} \varepsilon_p - \sum_{p,q=1}^{N/2} (2J_{pq} - K_{pq}) \]

\[ E_{HF} = E^0 + E^{(1)} \quad \text{UP TO THE FIRST ORDER OF R-S PERTURBATION THEORY} \]

\[ E = E^0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \]

\[ E_{HF} \quad \text{(SINGLE CONFIGURATION APPROXIMATION)} \]

\[ \text{ELECTRON CORRELATION BEYOND HARTREE-FOCK MODEL} \]
EXCITED DETERMINANTS

HARTREE-FOCK PROCEDURE $\Rightarrow$ K SPIN ORBITALS
FOR N-ELECTRON SYSTEM

$${k \choose N} = \frac{k!}{N!(k-N)!}$$

DETERMINANTS ONE OF WHICH DESCRIBES THE GROUND STATE WITHIN THE H-F MODEL

$$|\psi_0\rangle = |\chi_1, \chi_2, \ldots, \chi_a, \chi_b, \ldots, \chi_N\rangle$$ REFERENCE STATE

$$\chi_{N+1}, \ldots, \chi_K$$ - VIRTUAL STATES

CLASSIFICATION OF ALL THE OTHER DETERMINANTS BY HOW THEY DIFFER FROM THE REFERENCE STATE

$$|\psi_a^r\rangle = |\chi_1, \chi_2, \ldots, \chi_r, \chi_b, \ldots, \chi_N\rangle$$

A SINGLY EXCITED DETERMINANT

$$|\psi_{ab}^r\rangle = |\chi_1, \chi_2, \ldots, \chi_a, \chi_b, \chi_3, \ldots, \chi_N\rangle$$

DOUBLY EXCITED DETERMINANT

$${k \choose N}$$ DETERMINANTS:

HARTREE-FOCK GROUND STATE

SINGLY, DOUBLY, TRIPLY, QUADRUPLY...

... N-TUPLY EXCITED...

CONFIGURATIONS
CI: Configuration Interaction

N-electron basis functions: excited determinants

\[ \{ \chi_i \} = \text{complete set of functions} \]

\[ \Phi(x_1) = \sum_i a_i \chi_i(x_1) \quad \text{(exact)} \]

\[ \Phi(x_1 x_2) = \sum_i a_i \chi_i(x_1) \chi_i(x_2) \quad \text{functions of } x_2 \]

\[ \omega_i(x_2) = \sum_j b_{ij} \chi_j(x_2) \]

\[ \Phi(x_1 x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2) \]

But

\[ \Phi(x_1 x_2) = - \Phi(x_2 x_1) \Rightarrow \begin{cases} b_{ij} = -b_{ji} \\ b_{ii} = 0 \end{cases} \]

\[ \Phi(x_1 x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2) \]

\[ = \sum_{i \neq j} \sqrt{2} b_{ij} \chi_i \chi_j \quad \text{Slater determinant} \]

Arbitrary antisymmetric function can be exactly expanded in terms of determinants formed from a complete set of one-particle (variable) functions

\[ \{ \chi_i \} = \text{complete set of spin-orbitals} \]

Reference

\[ H = F + \text{singly exc.} + \text{doubly exc.} + \text{triply exc.} + \ldots \]

\[ |\Phi\rangle = c_0 |\psi_0\rangle + \sum_{\text{ra}} c_a |\psi_a\rangle + \sum_{\text{ab}} c_{ab} |\psi_{ab}\rangle + \sum_{\text{abc}} c_{abc} |\psi_{abc}\rangle + \ldots \]

"Configuration interaction"

\[ \Phi_{CI} = c_0 |\psi_0\rangle + c_s |\psi_s\rangle + c_D |\psi_D\rangle + c_T |\psi_T\rangle + c_Q |\psi_Q\rangle + \ldots \]
FULL CI:

EXACT EXPANSION:

\[ \Phi = c_0 \Psi_0 + \sum_{a r} c_r^{a} \Psi_r^{a} + \sum_{a b r s} c_r^{s t} \Psi_r^{s t} + \sum_{a b c d r s c d} c_r^{s t u} \Psi_r^{s t u} + \ldots \]

Each determinant is included only once.

Only coefficients are unknown.

\[ E_{\text{corr}} = E_{\text{FULL CI}} - E_{\text{HF}} \]

\( \text{\textup{\textsuperscript{\wedge}}} \) Exact value (negative since \( E_{\text{HF}} \) is always an upper bound to the exact energy).

\[ \langle \Phi | H | \Phi \rangle \] Matrix representation of the Hamiltonian in the basis of \( n \)-electron functions

\[ \Rightarrow \text{Full CI matrix} \Rightarrow \text{Eigenvalues} \]

Variational principle:

\[ c_0, c_a, c_{a b}, \ldots \] Linear variational parameters

\[ \min \{ E(c_0, c_a, \ldots) \} \Rightarrow \sum C (H_{k l} - E S_{k l}) = 0 \]

\( \text{\textup{\textsuperscript{\wedge}}} \) Unknown

For \( \Phi_{\text{FCI}} \) - The best energy one can get for a given one electron basis set.
1. There is no coupling between HF ground $\psi_0$ and single excitations $\langle \psi_0 | H | \psi_a \rangle = 0$ (but they do mix indirectly) 

Brillouin's theorem (valid for the ground state only)

$$
\langle \psi_0 | H | \psi_a \rangle = \langle a | H | a \rangle + \sum_b \langle ab | H | ab \rangle = \langle a | H | a \rangle = \varepsilon_{ar} = 0 \text{ when HF equations are solved}
$$

There is no direct contribution to the energy of the ground state due to single excitations (if virtual solutions are used to build singly excited configuration).

2. There is no coupling between $\psi_0$ and triplets and quadruples; why?

But $\langle DIHIQ \rangle \neq 0$ if: $\langle \psi_{rs} \mid H \mid \psi_{abcd} \rangle \{a_i b_i \} \in \{a, b, c, d\}$

3. Single excitations contribute to the energy indirectly, and their role is negligible in the description of energy but they are very important for a proper description of one-electron properties such as the dipole moment.

4. It is expected that the double excitations are the most important since they mix directly with $\psi_0$.

5. Calculations are performed using spin-adapted configurations (functions of good symmetry: $\hat{s}^2$).
COMMON APPROXIMATIONS TO FCI:

1. FULL CI IN RESTRICTED SPACE
   - ONLY TREAT VALENCE ELECTRONS
   - ONLY INCLUDE ACTIVE ELECTRONS
   - DISCARD VIRTUAL ORBITALS WITH VERY HIGH ENERGY:
     CAS-CI = COMPLETE ACTIVE SPACE CI

2. TRUNCATION OF THE CI WAVEFUNCTION EXPANSION
   
   CISD, CISDT, CISDTQ
   
   \[ |\Psi_{\text{CISD}}\rangle = a_0 |\Phi_0\rangle + a_s |1S\rangle + a_d |1D\rangle \]

   THE SIZE OF A PROBLEM GROWS FAST WITH THE SIZE OF A SYSTEM
   CANONICAL HARTREE-FOCK ORBITALS ARE NOT THE BEST BASIS
   FOR CI CALCULATIONS: SLOW CONVERGENCE OF THE EXPANSION
   LONG EXPANSIONS...

   WHICH FUNCTIONS TO USE IN ORDER TO AVOID THESE PROBLEMS?

   HOW TO OBTAIN THE BEST POSSIBLE RESULT? FROM THE
   VARIATIONAL PRINCIPLE IT IS CLEAR THAT THE BEST FUNCTIONS
   HAVE TO MINIMIZE THE ENERGY:

   **MCHF (MC SCF)**
   MULTICONFIGURATION HARTREE-FOCK
   BEYOND SINGLE CONFIGURATION APPROXIMATION!

   1. TRUNCATED CI EXPANSION
      
      \[ |\Psi_{\text{MCHF}}\rangle = \sum_I C_I |\Phi_I\rangle \]

   2. BOTH: EXPANSION COEFFICIENTS AND ORTHONORMAL ORBITALS OF |\Phi_I\rangle ARE OPTIMIZED!
### Examples:

#### He

- **Number of Conf.:** 1 (HF)  
  - \( E_{CI} \) (a.u.): -2.8617  
  - \( \Delta = E_{exc} - E_{CI} \): -0.0421

#### Be

- **Number of Conf.:** 1\(s^2\) 2\(s^2\) (HF)  
  - \( E_{exc} \): -2.9037

- **Number of Conf.:** \( 1s^2 2s^2 \) \( \left\{ CI \right\} \)  
  - \( E_{CI} \) (a.u.): -14.617  
  - \( C_1 = 0.95 \)

- **Number of Conf.:** \( 1s^2 2s^2 \) \( \left\{ CI \right\} \)  
  - \( E_{corr} \): 47%  
  - \( C_2 = 0.31 \)

- **Number of Config.:** \( \sum_{i} C_i \phi_i \)  
  - \( E_{exc} \): -14.661  
  - \( 94\% \) \( E_{corr} \)

- **Number of Config.:** \( \sum_{i} C_i \phi_i \)  
  - \( E_{exc} \): -14.667
TABLE 4-3 Convergence of an MCHF procedure for $1s^2 \, ^1S$ of He$^a$

<table>
<thead>
<tr>
<th>$m$</th>
<th>Configuration</th>
<th>$E_{\text{total}}$</th>
<th>$\Delta E_{\text{el}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$n = 2$</td>
<td>$n = 3$</td>
</tr>
<tr>
<td>1</td>
<td>$1s^2$</td>
<td>-2.861680</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$+2s^2$</td>
<td>-2.877997</td>
<td>-0.016317</td>
</tr>
<tr>
<td>3</td>
<td>$+3s^2$</td>
<td>-2.878871</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$+4s^2$</td>
<td>-2.878990</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$+2p^2$</td>
<td>-2.898554</td>
<td>-0.019564</td>
</tr>
<tr>
<td>6</td>
<td>$+3p^2$</td>
<td>-2.900150</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$+4p^2$</td>
<td>-2.900399</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$+3d^2$</td>
<td>-2.902179</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$+4d^2$</td>
<td>-2.902523</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$+4f^2$</td>
<td>-2.902909</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$+5g^2$</td>
<td>-2.903033</td>
<td></td>
</tr>
</tbody>
</table>

$E_{\text{exact}}^*$

$E - E_{\text{exact}}^*$

- $\Delta E_{\text{el}}(\text{max}) \text{ for } l = n-1$

TABLE 4-4 Mixing coefficients $c_{nj}$ for $1s^21S$ of H$^-$, He, Li$^+$ and the 11-configuration MCHF approximation

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$c_{nj}$</th>
<th>$c_{nj}$</th>
<th>$c_{nj}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^2$</td>
<td>0.972064</td>
<td>0.995967</td>
<td>0.998354</td>
</tr>
<tr>
<td>$2s^2$</td>
<td>-0.204931</td>
<td>-0.061750</td>
<td>-0.036953</td>
</tr>
<tr>
<td>$3s^2$</td>
<td>-0.013851</td>
<td>-0.007847</td>
<td>-0.005200</td>
</tr>
<tr>
<td>$4s^2$</td>
<td>-0.002458</td>
<td>-0.001707</td>
<td>-0.001198</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>0.110658</td>
<td>0.062046</td>
<td>0.041604</td>
</tr>
<tr>
<td>$3p^2$</td>
<td>0.015753</td>
<td>0.011044</td>
<td>0.007793</td>
</tr>
<tr>
<td>$4p^2$</td>
<td>0.003553</td>
<td>0.002691</td>
<td>0.001978</td>
</tr>
<tr>
<td>$3d^2$</td>
<td>-0.018226</td>
<td>-0.012793</td>
<td>-0.009070</td>
</tr>
<tr>
<td>$4d^2$</td>
<td>-0.004747</td>
<td>-0.003467</td>
<td>-0.002520</td>
</tr>
<tr>
<td>$4f^2$</td>
<td>0.005508</td>
<td>0.004103</td>
<td>0.002980</td>
</tr>
<tr>
<td>$5g^2$</td>
<td>-0.002487</td>
<td>-0.001894</td>
<td>-0.001374</td>
</tr>
</tbody>
</table>

$E^{HF}$: -0.487927 $H^-$ $-$2.861680 He $-$7.236415 Li$^+$
$E^{MCHF}$: -0.527510 $H^-$ $-$2.903033 He $-$7.279017 Li$^+$
$E^{exact}$: -0.527751 $H^-$ $-$2.903724 He $-$7.279913 Li$^+$

$E^{MCHF} - E^{exact}$: 0.000241 $H^-$ 0.000691 He 0.000906 Li$^+$

% correlation: 99.4% 98.4% 97.9%

---


Table II. Expansion coefficients for some states in $\psi(\alpha LS) = c_1 \Phi(\alpha LS) + c_2 \Phi(\alpha_2) + c_3 \Phi(\alpha_3) + \ldots$ where $|c_2| > |c_3| > \ldots$

<table>
<thead>
<tr>
<th>$\alpha LS$</th>
<th>$e$</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$c_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2s^2p^1p$</td>
<td>2$2s^2p$</td>
<td>$2p_3^13d_1, 2p^4_33d_2^2$</td>
<td>$2s_3d^1_1, 2s_3d^3_3$</td>
<td>$2s_3d^5_1, 2s_3d^3_3$</td>
<td>0.994</td>
<td>-0.069</td>
<td>0.034</td>
<td>-0.051</td>
</tr>
<tr>
<td>$2p^3p^3s$</td>
<td>2$2p^3p$</td>
<td>$2p^3_3d_1, 2p^6_3d_2$</td>
<td>$2p^3_3d_3, 2p^6_3d_2$</td>
<td>$2p^3_3d_5, 2p^6_3d_2$</td>
<td>0.991</td>
<td>0.095</td>
<td>0.094</td>
<td>0.093</td>
</tr>
<tr>
<td>$2s^2p^3p^3s$</td>
<td>2$2p^3p$</td>
<td>$2p^3_3d_1, 2p^6_3d_2$</td>
<td>$2p^3_3d_3, 2p^6_3d_2$</td>
<td>$2p^3_3d_5, 2p^6_3d_2$</td>
<td>0.989</td>
<td>0.093</td>
<td>0.063</td>
<td>-0.063</td>
</tr>
<tr>
<td>$2p^3p^3s$</td>
<td>2$2p^3p$</td>
<td>$2p^3_3d_1, 2p^6_3d_2$</td>
<td>$2p^3_3d_3, 2p^6_3d_2$</td>
<td>$2p^3_3d_5, 2p^6_3d_2$</td>
<td>0.987</td>
<td>0.140</td>
<td>0.053</td>
<td>-0.053</td>
</tr>
</tbody>
</table>

Table III. Wavelengths, $f$-values in the length ($f_l$) and velocity form ($f_v$), and transition probabilities (in $10^6$ $s^{-1}$) for some transitions in $Be I$ ($f$ – without $1s$ excitation, $f'$ – with $1s$ excitation)

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\lambda$(Å)</th>
<th>$f_l$</th>
<th>$f_v$</th>
<th>$f_l$</th>
<th>$f_v$</th>
<th>$A$ ($10^6$ $s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2s^2p^3$</td>
<td>0.1901</td>
<td>0.1801</td>
<td>0.1863</td>
<td>0.1792</td>
<td>0.1797</td>
<td>0.0997</td>
</tr>
<tr>
<td>$2s^2p^3$</td>
<td>0.1906</td>
<td>0.0952</td>
<td>0.1010</td>
<td>0.0952</td>
<td>0.1110</td>
<td>0.0175</td>
</tr>
<tr>
<td>$2s^2p^3$</td>
<td>0.2252</td>
<td>0.0919</td>
<td>0.0977</td>
<td>0.0913</td>
<td>0.0915</td>
<td>0.0363</td>
</tr>
<tr>
<td>$2s^2p^3$</td>
<td>0.2285</td>
<td>0.0723</td>
<td>0.0920</td>
<td>0.0718</td>
<td>0.0860</td>
<td>0.0277</td>
</tr>
<tr>
<td>$2s^2p^3$</td>
<td>0.2330</td>
<td>0.1063</td>
<td>0.1164</td>
<td>0.1066</td>
<td>0.1281</td>
<td>0.0078</td>
</tr>
<tr>
<td>$2s^2p^3$</td>
<td>0.2378</td>
<td>0.0477</td>
<td>0.1157</td>
<td>0.0477</td>
<td>0.1273</td>
<td>0.0034</td>
</tr>
</tbody>
</table>
Fig. 1. The spectral region 1100–1200 Å for 400 keV Be⁺–C foil excitation.

$2p^2 \, ^1D - 3p^2 \, ^1D$. In the wave-function expansion for $2p(1P)3p \, ^2D$ reported in Table VI, we see that the $3p^2$ and $2p^2$ components are indeed nearly equal in magnitude although opposite in sign. Thus the stationary condition of the multiconfiguration wave function.

Fig. 2. Partial energy-level diagram for core-excited Be II $^2L$ with the observed transitions indicated.
1. Show that \( \langle \psi_a^r | O_1 | \psi_b^s \rangle \), where \( O_1 \) is one-particle operator, for example: \( O_1 = h \)

\[
\begin{align*}
&= 0 \quad a \neq b, r \neq s \\
\langle \mathbf{r} | \mathbf{l} | \mathbf{h} | \mathbf{l} | \mathbf{s} \rangle & \quad a = b, r \neq s \\
-\langle \mathbf{b} | \mathbf{l} | \mathbf{h} | \mathbf{l} | \mathbf{a} \rangle & \quad a \neq b, r = s \\
\sum_c \{ \langle \mathbf{c} | \mathbf{l} | \mathbf{h} | \mathbf{l} | \mathbf{c} \rangle - \langle \mathbf{a} | \mathbf{l} | \mathbf{h} | \mathbf{l} | \mathbf{a} \rangle + \langle \mathbf{r} | \mathbf{l} | \mathbf{h} | \mathbf{r} \rangle & \quad a = b, r = s
\end{align*}
\]

2. IF \( |K\rangle = |X_1, X_2, X_3\rangle \) (Slater determinant)

Show that

\[
\langle K | H | K \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 3 | h | 3 \rangle + \langle 12 | h | 12 \rangle + \langle 13 | h | 13 \rangle + \langle 23 | h | 23 \rangle
\]

3. Find the energy for the determinant function that describes the following electron configurations:

- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)
- \( \begin{array}{c}
3 \\
2 \\
1
\end{array} \)