Electron correlation

- That part of electron–electron interaction, which is not included in the best IEA (Hartree-Fock) approximation
- The correlation energy:

$$E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{HF}\,.$$

- This includes the angular momentum coupling, but also other types of interactions (e.g. radial correlation)

- **One type of correlated wavefunction for the helium – the Hylleras wavefunction**
- **Contains explicitly the electron-electron distance as coordinate**

The variational method using more parameters

Hylleras

$$s = r_1 + r_2; \quad 0 \leq s \leq \infty \tag{10}$$

$$t = r_1 - r_2; \quad -\infty \leq \infty \tag{11}$$

$$u = r_{12}; \quad 0 \leq u \leq \infty. \tag{12}$$

Trial function

$$\phi_{s,t,u} = e^{-\alpha s} \sum_{i,j,k=0}^{n} c_{i,2j,k} s^i t^{2j} u^k. \tag{13}$$

$c_{i,2j,k}$, α - parameters

Frankowski and Pekeris - 1024 parameters

$$E_0 = -2,90372437703 \text{ hartree}. \tag{14}$$

– exact value

The configuration interaction (CI) method

- For a multielectron system the Hylleras wavefunction cannot be applied – N(N-1)/2 electron-electron coordinates
- In case of the CI method we use a trial function as a linear combination of several configurations
- c_i coefficients – variational parameters

$$\Phi = \sum_i c_i \phi_i .$$

Usually the $\{\phi_i\}$ basis is formed by the eigenfunctions of an approximate Hamiltonian, which can be written as a sum of one-electron operators. The basis is usually infinite. In practice we choose a basis set for which the expansion is rapidly convergent, and the coefficients c_i are negligible for greater values of i.

Let's keep the first n terms

$$\Phi = \sum_{i=1}^{n} c_i \phi_i$$

The functional

$$E[\Phi] = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

will depend on n linear parameters

$$E(c_1, c_2, \ldots, c_n) = \frac{\langle \sum_i c_i \phi_i | H | \sum_j c_j \phi_j \rangle}{\langle \sum_i c_i \phi_i | \sum_j c_j \phi_j \rangle} = \frac{\sum_{i,j} c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}}.$$

Here we have introduced the

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$

matrix elements and the

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

overlap integrals.

Using the Rayleigh–Ritz variational method we can write

$$\frac{\partial E}{\partial c_i^*} = \frac{\sum_j H_{ij} c_j (\sum_{i,j} c_i^* c_j S_{ij}) - \sum_j S_{ij} c_j (\sum_{i,j} c_i^* c_j H_{ij})}{(\sum_{i,j} c_i^* c_j S_{ij})^2} = 0,$$

where $i = \overline{1,n}$. Using the (15) formula we obtain

$$\sum_j c_j H_{ij} - \sum_j c_j S_{ij} E = 0,$$

or

$$\sum_j c_j (H_{ij} - S_{ij} E) = 0,$$

with $i = \overline{1,n}$. If we have an orthonormal basis set $S_{ij} = \delta_{ij}$, and the linear equation system reduces to an eigenvalue problem

$$\sum_j c_j(H_{ij} - \delta_{ij}E) = 0,$$

or in matrix form

$$\begin{bmatrix} H_{11}-E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22}-E & \cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn}-E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0.$$

The system has nonzero solutions only if the determinant of the matrix is zero

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22}-E & \cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn}-E \end{vmatrix} = 0. \qquad (23)$$

- From this n^{th} degree equation the eigeneregies (E) may be determined, and one may obtain also the expansion coefficients
- Each configuration should have the same symmetry, including the angular momentum state
- Possible methods:
  - direct method (solving the n^{th} degree equation for energies, ant then the linear equation system for the coefficients)
  - diagonalization of the matrix, obtaining the eigenvalues on the diagonal (e.g. Jacobi method)

We take as an example the 1^1S_0 ground state of the helium atom. We construct the state only from configurations with zero total spin and angular momentum, and the wavefunction depending on the spacial coordinates is symmetric under the interchange of the two electrons. So we can exclude from the beginning the $1s2p$ and $2s2p$ configurations.

Let us take the state as a linear combination of 3 configurations

$$1^1S_0 = c_1(1s^2) + c_2(1s2s) + c_3(2p^2). \tag{24}$$

Each configuration has to be written in a way to have the symmetry, spin and orbital momentum of the state. The first configuration is simply

$$(1s^2) = 1s(r_1)1s(r_2). \tag{25}$$

The second one has to be symmetrized

$$(1s2s) = \frac{1}{\sqrt{2}}[1s(r_1)2s(r_2) + 2s(r_1)1s(r_2)]. \tag{26}$$

In the third case we have to find a linear combination of the products to obtain a total orbital momentum $L = 0$. Using the (9) expansion we obtain

$$|1100\rangle = C^{00}_{1\text{-}111}|1\text{-}111\rangle + C^{00}_{1010}|1010\rangle + C^{00}_{111\text{-}1}|111\text{-}1\rangle, \tag{27}$$

or including the numerical values of the Clebsch-Gordan coefficients

$$(2p^2) = \frac{1}{\sqrt{3}}[2p_{-1}(\mathbf{r_1})2p_{+1}(\mathbf{r_2}) - 2p_0(\mathbf{r_1})2p_0(\mathbf{r_2}) + 2p_{+1}(\mathbf{r_1})2p_{-1}(\mathbf{r_2})], \tag{28}$$

where the low index of the orbitals stand for the magnetic quantum number.

A more specific example

PHYSICAL REVIEW VOLUME 110, NUMBER 5 JUNE 1, 1958

Approximate Wave Functions for the Ground State of Helium*

R. K. NESBET, *Boston University, Boston, Massachusetts*

AND

R. E. WATSON,† *Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received February 14, 1958)

Approximate ^1S electronic wave functions for the ground state of the helium atom have been obtained by the method of superposition of configurations. Parameters determining the radial factors of orbitals, with spherical harmonic angular factors up to $l=3$, were varied to minimize the calculated energy. For each choice of the ten parameters varied in this way, a complete calculation was carried out, involving the construction and diagonalization of the twenty-by-twenty configuration interaction matrix obtained from all independent ^1S functions determined by the ten independent orbital radial factors. The best energy obtained was -2.90276 atomic units, differing from the experimental value by 0.001 atomic unit.

The basis orbitals were chosen to be functions of the form

$$\eta_i(l,m,m_s) = R_{il}(r)\, Y_l{}^m(\theta,\phi) v(m_s),$$

where $Y_l{}^m$ is a normalized spherical harmonic and $v(m_s)$ is one of the two possible elementary spin functions. The radial functions were of the form

$$R_{il} = r^{A_i + l} e^{-a_i r},$$

TABLE II. The orthonormalized ψ's in terms of the η_i's.

Case (a)

$$\psi(s_1) = +1.94757\eta_1 + 2.81013\eta_2 - 0.06280\eta_3 - 0.29053\eta_4$$
$$\psi(s_2) = -15.38638\eta_1 + 10.15471\eta_2 + 41.31016\eta_3 - 36.05458\eta_4$$
$$\psi(s_3) = -2.05146\eta_1 + 7.07248\eta_2 + 149.53752\eta_3 - 69.60687\eta_4$$
$$\psi(s_4) = -71.67213\eta_1 + 4.47994\eta_2 + 440.18944\eta_3 + 33.98275\eta_4$$
$$\psi(p_1) = -11.07721\eta_5 + 20.08616\eta_6 - 63.32703\eta_7$$
$$\psi(p_2) = -5.29740\eta_5 + 20.81242\eta_6 - 161.35987\eta_7$$
$$\psi(p_3) = -108.43400\eta_5 - 18.13522\eta_6 + 270.76519\eta_7$$
$$\psi(d_1) = -107.39902\eta_8 + 52.74214\eta_9$$
$$\psi(d_2) = -338.53038\eta_8 + 40.40129\eta_9$$
$$\psi(f_1) = 138.59193\eta_{10}$$

Case (b)

$$\psi(s_1) = +4.73436\eta_1 + 0.12685\eta_2 + 0.88428\eta_3 + 0.07755\eta_4$$
$$\psi(s_2) = -3.03463\eta_1 + 6.31806\eta_2 - 11.64329\eta_3 + 6.60030\eta_4$$
$$\psi(s_3) = +2.47709\eta_1 + 18.07539\eta_2 - 34.24766\eta_3 + 10.89368\eta_4$$
$$\psi(s_4) = -24.54078\eta_1 + 79.30618\eta_2 - 64.43750\eta_3 + 14.20752\eta_4$$
$$\psi(p_1) = +7.26487\eta_5 - 22.48513\eta_6 + 27.81103\eta_7$$
$$\psi(p_2) = +10.26822\eta_5 - 75.21197\eta_6 + 47.38958\eta_7$$
$$\psi(p_3) = +81.52165\eta_5 - 155.44751\eta_6 + 63.09454\eta_7$$
$$\psi(d_1) = -35.01400\eta_8 + 91.17156\eta_9$$
$$\psi(d_2) = -148.57894\eta_8 + 135.34486\eta_9$$
$$\psi(f_1) = 157.48520\eta_{10}$$

TABLE III. The twenty ^1S wave functions constructed from the ψ's.

$$\Psi_1 = \psi(s_1;0),\psi(s_1;0)$$

$$\Psi_2 = (2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_2;0)+\psi(s_2;0),\psi(s_1;0)]$$

$$\Psi_3 = \psi(s_2;0),\psi(s_2;0)$$

$$\Psi_4 = (2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_3;0)+\psi($$

$$\Psi_5 = (2^{-\frac{1}{2}})[\psi(s_2;0),\psi(s_3;0)+\psi($$

$$\Psi_6 = \psi(s_3;0),\psi(s_3;0)$$

$$\Psi_7 = (2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_4;0)+\psi($$

$$\Psi_8 = (2^{-\frac{1}{2}})[\psi(s_2;0),\psi(s_4;0)+\psi($$

$$\Psi_9 = (2^{-\frac{1}{2}})[\psi(s_3;0),\psi(s_4;0)+\psi($$

$$\Psi_{10} = \psi(s_4;0),\psi(s_4;0)$$

$$\Psi_{11} = (3^{-\frac{1}{2}})[\psi(p_1;1),\psi(p_1;-1)-$$

$$\Psi_{12} = (6^{-\frac{1}{2}})[\psi(p_1;1),\psi(p_2;-1)-$$
$$+\psi(p_1;-1),\psi(p_2;1)+\psi($$
$$-\psi(p_2;0$$

$$\Psi_{13} = (3^{-\frac{1}{2}})[\psi(p_2;1),\psi(p_2;-1)-$$

$$\Psi_{14} = (6^{-\frac{1}{2}})[\psi(p_1;1),\psi(p_3;-1)-$$
$$+\psi(p_1;-1),\psi(p_3;1)+\psi($$
$$-\psi(p_3;0$$

$$\Psi_{15} = (6^{-\frac{1}{2}})[\psi(p_2;1),\psi(p_3;-1)-\psi(p_2;0),\psi(p_3;0)$$
$$\psi(p_2;-1),\psi(p_3;1)+\psi(p_3;1),\psi(p_2;-1)$$
$$-\psi(p_3;0),\psi(p_2;0)+\psi(p_3;-1),\psi(p_2;1)]$$

$$\Psi_{16} = (3^{-\frac{1}{2}})[\psi(p_3;1),\psi(p_3;-1)-\psi(p_3;0),\psi(p_3;0)$$
$$+\psi(p_3;-1)\psi(p_3;1)]$$

$$\Psi_{17} = (5^{-\frac{1}{2}})[\psi(d_1;2),\psi(d_1;-2)-\psi(d_1;1),\psi(d_1;-1)$$
$$+\psi(d_1;0),\psi(d_1;0)-\psi(d_1;-1),\psi(d_1;1)$$
$$+\psi(d_1;-2),\psi(d_1;2)]$$

$$\Psi_{18} = (10^{-\frac{1}{2}})[\psi(d_1;2),\psi(d_2;-2)-\psi(d_1;1),\psi(d_2;-1)$$
$$+\psi(d_1;0),\psi(d_2;0)-\psi(d_1;-1),\psi(d_2;1)$$
$$+\psi(d_2;2),\psi(d_1;-2)-\psi(d_2;1),\psi(d_1;-1)$$
$$+\psi(d_2;0),\psi(d_1;0)-\psi(d_2;-1),\psi(d_1;1)$$
$$+\psi(d_1;-2),\psi(d_2;2)+\psi(d_2;-2),\psi(d_1;2)]$$

$$\Psi_{19} = (5^{-\frac{1}{2}})[\psi(d_2;2),\psi(d_2;-2)-\psi(d_2;1),\psi(d_2;-1)$$
$$+\psi(d_2;0),\psi(d_2;0)-\psi(d_2;-1),\psi(d_2;1)$$
$$+\psi(d_2;-2),\psi(d_2;2)]$$

$$\Psi_{20} = (7^{-\frac{1}{2}})[\psi(f_1;3),\psi(f_1;-3)-\psi(f_1;2),\psi(f_1;-2)$$
$$+\psi(f_1;1),\psi(f_1;-1)-\psi(f_1;0),\psi(f_1;0)$$
$$+\psi(f_1;-1),\psi(f_1;1)-\psi(f_1;-2),\psi(f_1;2)$$
$$+\psi(f_1;-3),\psi(f_1;3)]$$

TABLE V. C_i's resulting from 20×20 diagonalizations.

i	Case (a)	Case (b)	i	Case (a)	Case (b)
1	+0.99596	+0.99596	11	+0.05010	+0.04420
2	−0.00026	+0.00179	12	−0.03086	−0.03478
3	−0.05671	−0.03329	13	+0.02259	+0.02655
4	+0.00175	+0.00153	14	−0.00165	+0.00362
5	+0.02220	+0.03943	15	+0.00521	−0.00847
6	−0.01229	−0.03198	16	+0.00362	+0.00581
7	−0.00011	−0.00107	17	−0.01211	−0.01173
8	−0.00019	−0.00602	18	+0.00291	+0.00407
9	+0.00113	+0.01095	19	−0.00325	−0.00464
10	−0.00075	−0.00607	20	+0.00411	+0.00399

action matrices. The final ^1S wave functions are a linear combination of the Ψ's of the form

$$\sum_i C_i \Psi_i,$$

and Table V gives the C_i's resulting from the 20×20

- **A more general method – multiconfiguration Hartree-Fock (MCHF)**
- **Hartree-Fock method, but with another set of variational parameters – the coefficients for each configuration**

PHYSICAL REVIEW A **76**, 054502 (2007)

Relativistic all-order and multiconfiguration Hartree-Fock calculations of the 4*d*-4*f* energy separation in Li I

M. S. Safronova
Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716, USA

C. Froese Fischer and Yu. Ralchenko
National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8422, USA
(Received 1 February 2007; published 9 November 2007)

We present a calculation of the 4*d*-4*f* energy separation in Li I using two advanced techniques in atomic structure theory, namely, the relativistic all-order method and the multiconfiguration Hartree-Fock (MCHF) method. The accuracy of our calculations was investigated by conducting a third-order many-body perturbation theory calculation that allowed us to evaluate the importance of fourth- and higher-order corrections. A large-scale MCHF calculation was performed using the active space method and the core-polarization approximation. The obtained results provide an important test of these methods against each other and are shown to agree with the most accurate available experimental data.

DOI: 10.1103/PhysRevA.76.054502 PACS number(s): 31.10.+z, 31.15.Md, 31.15.Ne, 31.25.Jf

in the calculations. In the MCHF approach, the atomic state is represented by an expansion over configuration state functions (CSFs)

$$\Psi(\gamma LS\pi) = \sum_i c_i \Phi(\gamma_i LS\pi), \sum_i c_i^2 = 1, \qquad (2)$$

where γ_i, L, S, and π denote, respectively, the configuration and its additional quantum numbers, the total orbital and spin momenta, and the parity. The CSFs are built from a basis of one-electron spin orbitals

$$\phi_{nlm_l m_s} = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \phi) \chi_{m_s}. \qquad (3)$$

The orbital radial functions $P_{nl}(r)$ along with the mixing coefficients of Eq. (2) are optimized together for a stationary solution. The ensuing expansions and orbitals are then used in a configuration interaction calculation that accounts for all

configurations was 26 580 for the 4*d* case and 32 346 for the 4*f* case.

Method B. In method A, the orbitals $4ln'l'n''l''$ with $n', n'' \geq 5$ in the CSF expansion are in fact the core-core correlation orbitals that interact with $1s^2$ in the case of $1s^2 4l$. Their contribution, however, cancels in the energy difference, at least to the first order, and therefore their importance for the present calculation is largely reduced. In order to accentuate those effects that contribute most to the energy splitting, with core polarization being the most prominent, we carried out another large-scale calculation of the $4d$-$4f$ separation. Hence, the correlation orbitals for the $1s^2$ core are first generated using the "natural orbital expansion" [18]

$$\Psi(1s^2\,{}^1S) = c_1\Phi(1s^2\,{}^1S) + c_2\Phi(2s^2\,{}^1S) + c_3\Phi(2p^2\,{}^1S) + c_4\Phi(3s^2\,{}^1S) + c_5\Phi(3p^2\,{}^1S).$$

With this correlated core, the $3d$, $4d$, and $4f$ orbitals were added to form $\Psi(1s^2\,{}^1S)nl$ and were optimized on the ${}^2D$ and ${}^2F$ terms. Then the $4s$, $4p$, and $n=5-7$, $l \leq 6$ orbitals entered the expansion only as core-polarization orbitals, i.e., at least one nl orbital with $n \leq 3$, $l \leq 1$ was present in the CFS's. During the optimization, the core orbitals were kept fixed. Finally, to check the effect of core-core correlations, the $n=8,9$, $l \leq 6$ orbitals were added with all three excitations included; however, only $n=8,9$ orbitals were allowed