Close encounters: The influence of electron coalescence on atomic wavefunctions.

David G. Ellis
The University of Toledo
Department of Physics and Astronomy

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(1) Atomic Structure and Spectra.
What we are trying to do.

(2) Electron Correlation.
One wavefunction for $N$ electrons.

(3) Cato’s Cusp and Hund’s Rule.
It’s important to consider close encounters.

(4) A Proposed Solution.
Try to add a new basis function to an already large set.
The starting multi-configuration wavefunction

Begin with a good approximate wavefunction for $N$ electrons:

$$
\Psi_0 = \sum_\gamma C_\gamma \Phi_\gamma
$$

The sum is over a number of configuration state functions (CSF). Each CSF $\Phi_\gamma$ is an antisymmetric function of the electron coordinates, specified by the label $\gamma$, which includes not only the electron configuration $\{ (n_1 l_1)^{w_1}, (n_2 l_2)^{w_2}, \ldots, (n_N l_N)^{w_N} \}$, but also the angular momentum coupling conditions and other quantities such as fractional parentage coefficients needed to specify the CSF.

$$
\Phi_\gamma(L, S, J, M) = \sum_{\alpha_1 \cdots \alpha_N} \langle \alpha_1 \cdots \alpha_N | \gamma, L, S, J, M \rangle \Phi(\alpha_1 \cdots \alpha_N)
$$

Here $\Phi(\alpha_1 \cdots \alpha_N)$ is a Slater determinant, i.e. an antisymmetrized direct product of $N$ single-particle Pauli wavefunctions (spin-orbitals):

$$
\Phi(\alpha_1 \cdots \alpha_N) = \mathcal{A} \phi_{\alpha_1(1)} \cdot \phi_{\alpha_2(2)} \cdots \phi_{\alpha_N(N)},
$$

with of course

$$
\phi_\alpha(\vec{r}, \sigma) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi) \chi_\mu(\sigma) \quad \text{and} \quad \alpha = \{n, l, m, \mu\}.
$$
The enhancement function for $N$ electrons

Given the best available orbital-based solution $\Psi_0$, we propose to construct an enhanced wavefunction

$$\Psi = \Psi_0 + \Psi'$$

where $\Psi'$ is an antisymmetric $N$-electron function which contains explicitly correlated two-electron functions. We want $\Psi'$ to be zero or very small everywhere except where any two electrons come close together, and to be orthogonal to each CSF in the original solution $\Psi_0$. We write an antisymmetrized function as:

$$\Psi' = \mathcal{A} \left\{ \Psi_{res}(1, 2, \cdots N-2)_{L_{r},S_{r}}, \psi'_{ij}(N-1, N)_{L_{p},S_{p}} \right\}_{L_{r},S_{r},J_{r},M_{r}}$$

Our initial trial form for the two-particle function is

$$\psi'_{ij}(1, 2)_{L,S} = \psi'_{L,M}(\vec{r}_1, \vec{r}_2) \phi(r_1, r_2, s)$$

where $s = r_{12}$ is the inter-electron distance, and $\psi'_{L,M}$ is the simplest possible function to give the electron pair the right total angular momentum. We can guarantee orthogonality by removing all the lower partial waves from our two-electron function, for example by the following definitions:

$$\phi_{\lambda}(r_1, r_2, s) = \phi(s) - \sum_{k=0}^{\lambda-1} \Gamma_k(r_1, r_2) P_k(\cos \theta_{12}) ,$$

with

$$\Gamma_k(r_1, r_2) = \frac{2k + 1}{2} \int_{-1}^{+1} \phi(s) P_k(\cos \theta_{12}) d \cos \theta_{12} .$$
Finding the change in energy

We want:
\[ \Delta E = \langle \Psi | H | \Psi \rangle - E_0 \]

We have:
\[ H = \sum_{ij} H_{ij} \]
\[ \Psi = \Psi_0 + \alpha \Psi' \]

\[ \langle H \rangle = \frac{E_0 + 2\alpha \langle \Psi_0 | H | \Psi' \rangle + \alpha^2 \langle \Psi' | H | \Psi' \rangle}{1 + \alpha^2} \]

Using the MCFP expansion we get:
\[ \langle \Psi_0 | H | \Psi' \rangle = \sum_{ij} C_{ij} \langle \psi_{ij}(1,2) | H_{12} | \psi'_p(1,2) \rangle \]

So now the problem is reduced to doing a two-electron integral.

But:
\[ \psi_{ij}(1,2) \text{ involves } r_1, \theta_1, \phi_1, \ r_2, \theta_2, \phi_2 \]
\[ \psi'_p(1,2) \text{ involves } \alpha, \beta, \gamma, \ r_1, r_2, \theta_1 2 \]
Calculation of $\langle \Psi^{(1L)} | H | \Phi^{(1L)} \rangle$

(1) $H$ is a symmetric spin-independent scalar two-body operator, for example the non-relativistic hamiltonian.

(2) $| \Phi^{(1L)} \rangle$ is a two-electron spin-singlet state:

$$\Phi_{LM}(\vec{r}_1, \vec{r}_2) = \sum_{K} (-1)^{(M+K)} \phi_{LK}(r_1, r_2, \theta) D_{MK}^L(\alpha, \beta, \gamma)$$

Here $\theta$ is the angle between the vectors $\vec{r}_1, \vec{r}_2$, the Euler angles $\alpha, \beta, \gamma$ specify the orientation of the plane containing the two vectors, and $D_{MK}^L$ is the Wigner D-function.

(3) $| \Psi^{(1L)} \rangle$ is a two-electron spin-singlet state represented by an orbital-based LS-coupled function defined by

$$\Psi_{l_1l_2LM}(\vec{r}_1, \vec{r}_2) = \sum_{m_1, m_2} \langle l_1, m_1; l_2, m_2 | L, M \rangle \psi_{l_1m_1}(\vec{r}_1) \psi_{l_2m_2}(\vec{r}_2)$$

Now we can transform this also to the variables $(r_1, r_2, \theta, \alpha, \beta, \gamma)$:

$$\Psi_{l_1l_2LM}(\vec{r}_1, \vec{r}_2) = \sum_{K} (-1)^{M+K} F_{l_1l_2}^{LK}(\theta) R_{l_1}(r_1) R_{l_2}(r_2) D_{MK}^L(\alpha, \beta, \gamma)$$

with the definition

$$F_{l_1l_2}^{LK}(\theta) = \sum_{m_1m_2} \langle l_1 m_1, l_2 m_2 | LK \rangle Y_{l_1m_1}(\pi/2, -\theta/2) Y_{l_2m_2}(\pi/2, \theta/2)$$
The two-electron hamiltonian

The non-relativistic hamiltonian for two electrons in the field of a fixed nucleus of charge $Z$ can be written

\[ H_{\text{nr}} = H_{\text{rad}} + H_{\text{ang}} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \]

\[ H_{\text{rad}} = -\frac{1}{2r_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2r_2} \frac{\partial^2}{\partial r_2^2} \]

\[ H_{\text{ang}} = \frac{1}{2r_1^2} L_1^2 + \frac{1}{2r_2^2} L_2^2. \]

We must rewrite $H_{\text{ang}}$ in terms of the coordinates $(\alpha, \beta, \gamma, \theta)$. First we define the sum and difference of the angular momenta $\vec{L} = \vec{L}_1 + \vec{L}_2$ and $\vec{\Delta} = \vec{L}_1 - \vec{L}_2$, and the components in the rotated frame $\vec{L}'$. The shift operators are $L_\pm = L_x \pm iL_y$ and $L'_\pm = L'_x \pm iL'_y$. These have the following action on the Wigner D-functions:

\[ L^2 D^L_{MK}(\alpha, \beta, \gamma) = L(L+1) D^L_{MK}(\alpha, \beta, \gamma) \]

\[ L_z D^L_{MK}(\alpha, \beta, \gamma) = M D^L_{MK}(\alpha, \beta, \gamma) \]

\[ L_\pm D^L_{MK}(\alpha, \beta, \gamma) = C^\pm_{LM} D^L_{M\pm1,K}(\alpha, \beta, \gamma) \]

\[ L'_z D^L_{MK}(\alpha, \beta, \gamma) = K D^L_{MK}(\alpha, \beta, \gamma) \]

\[ L'_\pm D^L_{MK}(\alpha, \beta, \gamma) = C^\pm_{LK} D^L_{M,K\pm1}(\alpha, \beta, \gamma) \]

The result for the angular part of the kinetic energy operator is

\[ H_{\text{ang}} = \frac{1}{8} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) (L^2 + \Delta^2) + \frac{1}{4} \left( \frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \vec{L} \cdot \vec{\Delta} \]

\[ \Delta^2 = -4 \csc \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \frac{2 - \sin^2 \theta}{\sin^2 \theta} (L^2 - L'_z^2) + \frac{\cos \theta}{\sin^2 \theta} (L'_+^2 + L'_-^2) \]

\[ \vec{L} \cdot \vec{\Delta} = i \left( \frac{\partial}{\partial \theta} + \frac{\cos \theta}{2 \sin \theta} \right) L'_z - \frac{i}{4 \sin \theta} (L'_+^2 - L'_-^2) \]
The integrations which must be done

To write the necessary integrals for matrix elements using Euler angles \((\alpha, \beta, \gamma)\) and internal coordinates \((r_1, r_2, \theta)\), define

\[
\int d^3 r_1 \int d^3 r_2 = \int d\tau \int d\omega \\
\int d\omega = \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta \, d\beta \int_0^{2\pi} d\gamma \\
\int d\tau = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\pi \sin \theta \, d\theta.
\]

Now we can use the orthonormality integral for the Wigner functions

\[
\frac{1}{8\pi^2} \int D_{M'K'}^L(\alpha, \beta, \gamma) D_M^L(\alpha, \beta, \gamma)^* \, d\omega = \frac{\delta_{L'LL} \delta_{M'M} \delta_{K'K}}{2L+1}
\]

to write our interaction matrix element in terms of

\[
\int R_{l_1}(r_1) R_{l_2}(r_2) \mathcal{H}_{l_1l_2}^{(L)}(r_1, r_2, \theta) \phi_\lambda(r_1, r_2, \theta) \, d\tau
\]

where we have defined

\[
\mathcal{H}_{l_1l_2}^{(L)}(r_1, r_2, \theta) \equiv \sum_{K'K} F_{l_1l_2}^{L_{K'K}} \cdot \int D_{MK'}^L \, \mathcal{H}_{nr} \, D_M^L \, d\omega \cdot F_{0L}^{L_{K'}}
\]

Here \(\mathcal{H}_{nr}\) is the nonrelativistic hamiltonian operator for the two-electron system. It contains derivatives which act on the remaining variables \((r_1, r_2, \theta)\) in the enhancement function \(\phi_\lambda(r_1, r_2, \theta)\), in addition to the derivatives with respect to the Euler angles, which we work out analytically.
Finally the crucial function is

\[
\mathcal{H}_{l_1 l_2}^{(L)}(r_1, r_2, \theta) = \frac{1}{2} \sqrt{[l_1 l_2]/[L]} \langle l_1 0, l_2 0 | L 0 \rangle P_{l_1} (\cos \theta) \\
\times \left\{ H_{\text{rad}} + U - \frac{1}{2} g + D_{\theta}^2 + \frac{L(L + 1)}{24} \left[ 2g_+ (1 + 2 \csc^2 \theta) - g_- \right] \right\} \\
- \frac{\pi i}{4} \sqrt{L(L + 1)/3} (-1)^{l_1} [l_1 l_2]^{1/2} \langle l_1 0, l_2 0 | L 0 \rangle \left\{ l_1 \ l_1 \ 1 \right\} \\
\times F_{l_1 l_1}^{10} (\theta) (2g_+ - g_-) (\cot \theta + 2 \frac{\partial}{\partial \theta}) \\
+ \frac{\pi (-1)^{L+1} \sqrt{l_2}}{24 \sqrt{5}} \frac{(2L + 3)!}{(2L - 2)!} \sum_J \langle l_2 0, L 0 | J 0 \rangle \left\{ l_1 \ l_2 \ L \right\} \left\{ L \ 2 \ J \right\} \\
\times F_{l_1 l_1}^{20} (\theta) (2g_+ \cot^2 \theta + g_-) \\
+ \frac{\pi}{4} (-1)^L \sqrt{l_2} \sum_J \langle l_2 0, L 0 | J 0 \rangle \left\{ l_1 \ l_2 \ L \right\} \left\{ L \ 2 \ J \right\} \\
\times \csc \theta \left[ F_{J l_1}^{22} (\theta) (2g_+ \cot \theta - ig_-) + F_{J l_1}^{2-2} (\theta) (2g_+ \cot \theta + ig_-) \right].
\]

Here we have used the definitions

\[
U = -Z/r_1 - Z/r_2 + (N - 1)/r_{12} \\
g_\pm = 1/r_1^2 \pm 1/r_2^2
\]

Note that \( H_{\text{rad}} \) and \( D_{\theta}^2 \) contain derivatives which act on \( \phi_\lambda (r_1, r_2, \theta) \) and which must be worked out analytically, and then the three-dimensional integral \( \int d\tau \) must be done numerically.
(1) **Extend to pairs with** \( L > 0 \).

This is what I’m working on now. The equations that must be programmed are much more complicated.

(2) **Make the integrals more efficient.**

The three-dimensional integrals are very time-consuming.

(3) **Make the method relativistic.**

The whole thing needs to be redone using *Dirac* wavefunctions.

(4) **Transition probabilities.**

We don’t want just wavefunctions, we need to be able to calculate transition probabilities and other atomic properties. This will involve working out more three-dimensional integrals.