# 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*** $\{(n_1 l_1)^{w_1}, (n_2 l_2)^{w_2}, \cdots (n_{N_g} l_{N_g})^{w_{N_g}}\}$, but also the angular momentum coupling conditions and other quantities such as fractional parentage coefficients needed to specify the CSF.

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

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:

$$\Psi' = \mathcal{A}\ \left\{ \Psi_{res}(1,2,\cdots N-2)_{L_r,S_r}\ ,\ \psi'_{ij}(N-1,N)_{L_p,S_p} \right\}_{L,S,J,M}$$

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:**

$$\Delta E \;=\; \langle\, \Psi \mid \mathbf{H} \mid \Psi \,\rangle \;-\; E_0$$

**We have:**

$$\mathbf{H} = \sum_{ij}\; H_{ij}$$

$$\Psi = \Psi_0 + \alpha\; \Psi'$$

$$\langle\, \mathbf{H} \,\rangle = \frac{E_0 + 2\alpha\; \langle\, \Psi_0 \mid \mathbf{H} \mid \Psi' \,\rangle \;+ \alpha^2\; \langle\, \Psi' \mid \mathbf{H} \mid \Psi' \,\rangle}{1 + \alpha^2}$$

**Using the MCFP expansion we get:**

$$\langle\, \Psi_0 \mid \mathbf{H} \mid \Psi' \,\rangle \;= \sum_{ij} C_{ij}\; \Big\langle\, \psi_{ij}(1,2) \mid H_{12} \mid \psi'_p(1,2) \,\Big\rangle$$

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

**But:**

$$\begin{aligned} \psi_{ij}(1,2) \quad &\text{involves} \quad r_1, \theta_1, \phi_1,\; r_2, \theta_2, \phi_2 \\ \psi'_p(1,2) \quad &\text{involves} \quad \alpha, \beta, \gamma,\; r_1, r_2, \theta_1 2 \end{aligned}$$

# Calculation of $\langle\, \mathbf{\Psi}(\,^1L) \,|\, \mathbf{H} \,|\, \mathbf{\Phi}(\,^1L) \,\rangle$

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

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

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

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 $\mathcal{D}^L_{MK}$ is the Wigner D-function.

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

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

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

$$\Psi_{l_1 l_2 LM}(\vec{r}_1, \vec{r}_2) = \sum_K (-1)^{M+K} F^{LK}_{l_1 l_2}(\theta) R_{l_1}(r_1) R_{l_2}(r_2) \mathcal{D}^L_{MK}(\alpha, \beta, \gamma)$$

with the definition

$$F^{LK}_{l_1 l_2}(\theta) = \sum_{m_1 m_2} \langle\, l_1 m_1, l_2 m_2 \,|\, LK \,\rangle\, Y_{l_1 m_1}(\pi/2, -\theta/2) Y_{l_2 m_2}(\pi/2, \theta/2)$$

# The two-electron hamiltonian

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

$$\begin{aligned}
\mathbf{H}_{\rm nr} &= \mathbf{H}_{\rm rad} + \mathbf{H}_{\rm ang} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\,. \\
\mathbf{H}_{\rm rad} &= -\frac{1}{2r_1}\frac{\partial^2}{\partial r_1^2} r_1 - \frac{1}{2r_2}\frac{\partial^2}{\partial r_2^2} r_2 \\
\mathbf{H}_{\rm ang} &= \frac{1}{2r_1^2}\mathbf{L}_1^2 + \frac{1}{2r_2^2}\mathbf{L}_2^2\,.
\end{aligned}$$

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

$$\begin{aligned}
\mathbf{L}^2\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) &= L(L+1)\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) \\
\mathbf{L}_z\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) &= M\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) \\
\mathbf{L}_\pm\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) &= C^\pm_{LM}\, \mathcal{D}^L_{M\pm1,K}(\alpha,\beta,\gamma) \\
\mathbf{L}'_z\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) &= K\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) \\
\mathbf{L}'_\pm\, \mathcal{D}^L_{MK}(\alpha,\beta,\gamma) &= C^\pm_{LK}\, \mathcal{D}^L_{M,K\pm1}(\alpha,\beta,\gamma)
\end{aligned}$$

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

$$\begin{aligned}
\mathbf{H}_{\rm ang} &= \frac{1}{8}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)(\mathbf{L}^2 + \mathbf{\Delta}^2) + \frac{1}{4}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right)\vec{\mathbf{L}}\cdot\vec{\mathbf{\Delta}} \\
\mathbf{\Delta}^2 &= -4\csc\theta \frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{2-\sin^2\theta}{\sin^2\theta}\left(\mathbf{L}^2 - \mathbf{L}'^2_z\right) + \frac{\cos\theta}{\sin^2\theta}\left(\mathbf{L}'^2_+ + \mathbf{L}'^2_-\right) \\
\vec{\mathbf{L}}\cdot\vec{\mathbf{\Delta}} &= i\left(\frac{\partial}{\partial\theta} + \frac{\cos\theta}{2\sin\theta}\right)\mathbf{L}'_z - \frac{i}{4\sin\theta}\left(\mathbf{L}'^2_+ - \mathbf{L}'^2_-\right)
\end{aligned}$$

## 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

$$\begin{aligned} \int d^3r_1 \int d^3r_2 &= \int d\tau \int d\omega \\ \int d\omega &= \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta \, d\beta \int_0^{2\pi} d\gamma \\ \int d\tau &= \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \int_0^{\pi} \sin\theta \, d\theta \, . \end{aligned}$$

Now we can use the orthonormality integral for the Wigner functions

$$\frac{1}{8\pi^2} \int \mathcal{D}^{L'}_{M'K'}(\alpha,\beta,\gamma)^* \mathcal{D}^{L}_{MK}(\alpha,\beta,\gamma) \, d\omega = \frac{\delta_{L'L}\delta_{M'M}\delta_{K'K}}{2L+1}$$

to write our interaction matrix element in terms of

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

where we have defined

$$\mathcal{H}^{(L)}_{l_1 l_2}(r_1, r_2, \theta) \equiv \sum_{K'K} {F^{LK'}_{l_1 l_2}}^* \cdot \int {\mathcal{D}^L_{MK'}}^* \, \mathbf{H}_{\rm nr} \, \mathcal{D}^L_{MK} d\omega \cdot F^{LK}_{0L}$$

Here $\mathbf{H}_{\rm nr}$ 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

$$
\begin{aligned}
\mathcal{H}^{(L)}_{l_1 l_2}(r_1, r_2, \theta) =& \tfrac{1}{2}\sqrt{[l_1 l_2]/[L]}\, \langle\, l_1 0, l_2 0 \mid L0 \,\rangle\, P_{l_1}(\cos\theta) \\
& \times \left\{ H_{rad} + U - \tfrac{1}{2} g_+ D_\theta^2 + \frac{L(L+1)}{24} \left[ 2g_+(1 + 2\csc^2\theta) - g_- \right] \right\} \\
& - \frac{\pi i}{4} \sqrt{L(L+1)/3}\, (-1)^{l_1} [l_1 l_2]^{1/2}\, \langle\, l_1 0, l_2 0 \mid L0 \,\rangle \begin{Bmatrix} l_1 & l_1 & 1 \\ L & L & l_2 \end{Bmatrix} \\
& \qquad \times F^{10}_{l_1 l_1}(\theta)(2g_+ - g_-)(\cot\theta + 2\frac{\partial}{\partial\theta}) \\
& + \frac{\pi(-1)^{L+1}\sqrt{[l_2]}}{24\sqrt{5}} \sqrt{\frac{(2L+3)!}{(2L-2)!}} \sum_J \langle\, l_2 0, L0 \mid J0 \,\rangle \begin{Bmatrix} l_1 & l_2 & L \\ L & 2 & J \end{Bmatrix} \\
& \qquad \times F^{20}_{J l_1}(\theta)(2g_+ \cot^2\theta + g_-) \\
& + \frac{\pi}{4}(-1)^L [L] L(L+1) \sqrt{[l_2]} \begin{Bmatrix} 2 & L & L \\ L & 1 & 1 \end{Bmatrix} \sum_J \langle\, l_2 0, L0 \mid J0 \,\rangle \begin{Bmatrix} l_1 & l_2 & L \\ L & 2 & J \end{Bmatrix} \\
& \qquad \times \csc\theta \left[ F^{22}_{J l_1}(\theta)(2g_+ \cot\theta - i g_-) + F^{2\,-2}_{J l_1}(\theta)(2g_+ \cot\theta + i g_-) \right] .
\end{aligned}
$$

Here we have used the definitions

$$
\begin{aligned}
U &= -Z/r_1 - Z/r_2 + (N-1)/r_{12} \\
g_\pm &= 1/r_1^2 \pm 1/r_2^2
\end{aligned}
$$

Note that $H_{rad}$ 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.

## Current and future work

### (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.