Further details on the calculation of matrix elements in "The Coulson-Fischer + r_{12} wavefunction for H_2" by Nick J. Clarke, David L. Cooper, Joseph Gerratt and Mario Raimondi, Molecular Physics 81, 921-935 (1994).

The calculations were performed in confocal elliptical coordinates (ξ,η,ϕ) defined as:

$$\xi = \frac{(r_a + r_b)}{R}; \qquad \eta = \frac{(r_a - r_b)}{R};$$

ϕ is the angle between the AeB plane and the yz plane. A and B are the two nuclei, which define the z axis, and e is an electron. The integration ranges are: $+1 \le \xi \le \infty$; $-1 \le \eta \le +1$; $0 \le \phi \le 2\pi$.

r_a and r_b are easily written in terms of ξ and η. Expressions for x, y and z are given in the paper. This leaves only the volume element and r_{12}.

$$dxdydz = \frac{R^3}{8}(\xi^2 - \eta^2)\, d\xi\, d\eta\, d\phi$$

$$r_{12}^2 = \frac{R^2}{4}[\xi_1^2 + \eta_1^2 + \xi_2^2 + \eta_2^2 - 2\xi_1\eta_1\xi_2\eta_2 - 2 - 2\{(\xi_1^2 - 1)(1-\eta_1^2)(\xi_2^2 - 1)(1-\eta_2^2)\}^{\frac{1}{2}}\cos(\phi_1 - \phi_2)]$$

Substituting these expressions into the matrix elements below allows for their solution by standard numerical integration procedures.

The Born-Oppenheimer Hamiltonian (minus the internuclear potential) is:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{12}$$

$$\hat{T} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2; \quad \hat{V} = -\frac{1}{r_{a_1}} - \frac{1}{r_{a_2}} - \frac{1}{r_{b_1}} - \frac{1}{r_{b_2}}; \quad \hat{V}_{12} = \frac{1}{r_{12}}$$

Writing the Coulson-Fischer+r_{12} wavefunction as $\Psi_{CF+r_{12}} = \left(\Psi_{HL} + c\Psi_{ION}\right)\left(1 + pr_{12}\right)$ and ignoring the parameters c and p, which are optimised later, the Hamiltonian matrix elements required are:

$$\langle \Psi_i r_{12}^m | \hat{T} | \Psi_j r_{12}^n \rangle$$

$$\langle \Psi_i r_{12}^m | \hat{V} | \Psi_j r_{12}^n \rangle \qquad \text{i and j = HL or ION;} \quad \text{m and n = 0 or 1}$$

$$\langle \Psi_i r_{12}^m | \hat{V}_{12} | \Psi_j r_{12}^n \rangle$$

The matrix elements involving $\hat{V}$ and $\hat{V}_{12}$ are evaluated directly by the relevant substitutions to confocal elliptical coordinates given above, leaving only: $\langle \Psi_i r_{12} | \hat{T} | \Psi_j \rangle$ and $\langle \Psi_i r_{12} | \hat{T} | \Psi_j r_{12} \rangle$.

Firstly

$$\langle \Psi_i r_{12} | \hat{T} | \Psi_j \rangle = -\tfrac{1}{2} \langle \Psi_i r_{12} | \nabla_1^2 + \nabla_2^2 | \Psi_j \rangle$$

$\boldsymbol{\Psi}_{HL}$ and $\boldsymbol{\Psi}_{ION}$ are both symmetric in the coordinates of the two electrons, therefore:

$$\langle \Psi_i r_{12} | \hat{T} | \Psi_j \rangle = -\langle \Psi_i r_{12} | \nabla_1^2 | \Psi_j \rangle .$$

Denoting $1s_a(1)$ as a_1 etc and taking i and j as HL, for example

$$\langle \Psi_{HL} r_{12} | \hat{T} | \Psi_{HL} \rangle = -\langle (a_1 b_2 + b_1 a_2) r_{12} | \nabla_1^2 | (a_1 b_2 + b_1 a_2) \rangle$$

$$= -2 \langle (a_1 b_2 + b_1 a_2) r_{12} \cdot b_2 | \nabla_1^2 | a_1 \rangle$$

since operating on a_1 or b_1 with ∇_1^2 produces identical results. The orbital a_1 is a standard 1*s* STO so

$$\nabla_1^2 a_1 = \left(\zeta^2 - \frac{2\zeta}{r_{a_1}} \right) a_1$$

where ζ is of course the STO exponent, giving:

$$\langle \Psi_{HL} r_{12} | \hat{T} | \Psi_{HL} \rangle = -2 \langle (a_1 b_2 + b_1 a_2) | r_{12} | a_1 b_2 \left(\zeta^2 - \frac{2\zeta}{r_{a_1}} \right) \rangle .$$

Substitution of confocal elliptical coordinates now renders this soluble.

Finally we have matrix elements of the form:

$$\langle \Psi_{HL} r_{12} | \hat{T} | \Psi_{HL} r_{12} \rangle = -2 \langle \Psi_{HL} r_{12} \cdot b_2 | \nabla_1^2 | a_1 r_{12} \rangle ,$$

using the same reasoning as before. Analysis gives

$$\nabla_1^2 a_1 r_{12} = a_1 \nabla_1^2 r_{12} + r_{12} \nabla_1^2 a_1 + 2(\nabla_1 r_{12} \cdot \nabla_1 a_1)$$

$$\nabla_1^2 r_{12} = \frac{2}{r_{12}}$$

$$\nabla_1^2 a_1 = \left(\zeta^2 - \frac{2\zeta}{r_{a_1}} \right) a_1$$

$$\nabla_1 r_{12} = \frac{1}{r_{12}} [(x_1 - x_2)\mathbf{i} + (y_1 - y_2)\mathbf{j} + (z_1 - z_2)\mathbf{k}]$$

$$\nabla_1 a_1 = -\frac{\zeta a_1}{r_{a_1}} [x_{a_1}\mathbf{i} + y_{a_1}\mathbf{j} + z_{a_1}\mathbf{k}]$$

Combining these all together gives:

$$\langle \Psi_{HL} r_{12} | \hat{T} | \Psi_{HL} r_{12} \rangle = -2 \langle \Psi_{HL} a_1 b_2 [2 + r_{12}^2 \left(\zeta^2 - \frac{2\zeta}{r_{a_1}} \right) -$$

$$\frac{2\zeta}{r_{a_1}} \{ x_1 (x_1 - x_2) + y_1 (y_1 - y_2) + \left(z_1 + \frac{R}{2} \right) (z_1 - z_2) \}] \rangle$$

Again, substitution of the confocal elliptical equivalents of these variables makes this integral soluble.