Perturbation Theory for He: The ($1/r_{12}$) Integral **Chemistry BC3253x**
(adapted from Goodisman, *Contemporary Quantum Chemistry*)

Working in atomic units, the exact Hamiltonian is $\mathbf{H_1 + H_2 + (1/r_{12})}$.

The zeroth-order wavefuction $\psi^0 = \psi_1 \psi_2$ where ψ_k is the (real) 1s eigenfunction for H_k:

$$\boldsymbol{\psi_k = (z^3/\pi)^{1/2} \exp(-Zr_k)}$$

According to perturbation theory, $\boldsymbol{\Delta E = \int \psi_1 \psi_2 \; (1/r_{12}) \; \psi_1 \psi_2 \; d\tau}$

$d\tau$ is a six-dimensional integral: (r, θ, φ) for each electron.

From the law of cosines, $r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\alpha$ where α is the angle between vectors r_1 and r_2. The orientation of the polar axes is arbitrary. A trick for doing the integrals is to set the polar axis for electron 2 in the direction of electron 1. Thus α in the law of cosines expression for r_{12} will simply be θ_2. The ψ's don't involve angles, so we can start with the integral over θ_2:

$$\int_0^{\pi}\left(r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2\right)^{-1/2} \sin\theta_2 d\theta_2 = \left[\frac{\left(r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2\right)^{1/2}}{-(1/2)r_1r_2}\right]_0^{\pi}$$

$$= \left[\frac{r_1 + r_2 - |r_1 - r_2|}{r_1r_2}\right]$$

The absolute value comes from taking the positive (physically meaningful) square root of ($r_1^2 + r_2^2 - 2r_1r_2$). If $r_1 > r_2$ this is ($r_1 - r_2$) and if $r_2 > r_1$ it is ($r_2 - r_1$). So when $r_2 > r_1$, the expression is equal to ($2/r_1$) while when $r_2 < r_1$ it is equal to ($2/r_2$)

Since the wavefunctions and the term in square brackets involve only r's, the other angular integrals are trivial, giving $(2)(2\pi)(2\pi) = 8\pi^2$. We are left with the integrals over r_1 and r_2.

$$\Delta E = (8\pi^2)\int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \left(\frac{Z^3}{\pi}\right)^2 \left[\frac{r_1 + r_2 - |r_1 - r_2|}{r_1r_2}\right] e^{-2Zr_1} e^{-2Zr_2}$$

Break the integral into two parts:

$$\Delta E = (16Z^6)\int_0^{\infty} r_1\, e^{-2Zr_1} \left\{\int_0^{r_1} r_2^2 e^{-2Zr_2} dr_2 + r_1 \int_{r_1}^{\infty} r_2\, e^{-2Zr_2} dr_2\right\} dr_1$$

$$\Delta E = (16Z^6)\int_0^{\infty} r_1\, e^{-2Zr_1} \left\{\left[\frac{e^{-2Zr_2}}{(2Z^3)}(-4Z^2r_2^2 - 4Zr_2 - 2)\right]_0^{r_1} + r_1\left[\frac{e^{-2Zr_2}}{(4Z^2)}(-2Zr_2 - 1)\right]_{r_1}^{\infty}\right\} dr_1$$

$$\Delta E = (16Z^6)\int_0^{\infty} r_1\, e^{-2Zr_1} \left\{\frac{e^{-2Zr_1}}{8Z^3}(-2Zr_1 - 2) + \frac{2}{8Z^3}\right\} dr_1$$

$$\Delta E = (2Z^3)\int_0^{\infty} r_1\, e^{-2Zr_1} \left\{e^{-2Zr_1}(-2Zr_1^2 - 2r_1) + 2r_1\right\} dr_1 = (2Z^3)\left\{\frac{-4Z}{(4Z)^3} - \frac{2}{(4Z)^2} + \frac{2}{(2Z)^2}\right\} = \frac{5Z}{8}$$

(Microsoft equation editor does a sloppy job with subscripts in exponents).