Solution: CID for H_2

1. *"Calculate the HF energy"*

$$E_{\text{HF}} = 2h_1 + (11|11) = -1.8310$$

2. *"Calculate the ground state CID energy"*

$$\mathbf{H}_{\text{CID}} = \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} = \begin{pmatrix} 2h_1 + (11|11) & (12|12) \\ (12|12) & 2h_2 + (22|22) \end{pmatrix}$$

$$E_{\text{CID}} = \frac{H_{11} + H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2)}}{2} = -1.8516 \text{ or } -0.2331$$

3. *"Calculate the correlation energy"*

$$E_c = E_{\text{CID}} - E_{\text{HF}} = -1.8516 - (-1.8310) = -0.0206$$

Rayleigh-Schrödinger perturbation theory

Let's assume we want to find Ψ_0 and E_0, such as

$$(\mathbf{H}^{(0)} + \lambda \mathbf{H}^{(1)})\Psi_0 = E_0\,\Psi_0$$

and that we know

$$\boxed{\mathbf{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}, \qquad n = 0, 1, 2, \ldots, \infty}$$

Let's expand Ψ_0 and E_0 in term of λ:

$$E_0 = \lambda^0\, E_0^{(0)} + \lambda^1\, E_0^{(1)} + \lambda^2\, E_0^{(2)} + \lambda^3\, E_0^{(3)} + \ldots$$

$$\Psi_0 = \lambda^0\, \Psi_0^{(0)} + \lambda^1\, \Psi_0^{(1)} + \lambda^2\, \Psi_0^{(2)} + \lambda^3\, \Psi_0^{(3)} + \ldots$$

such as (intermediate normalization)

$$\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle = 1 \qquad \langle \Psi_0^{(0)} | \Psi_0^{(k)} \rangle = 0, \quad k = 1, 2, \ldots, \infty$$

Rayleigh-Schrödinger perturbation theory (Part 1)

"Can you find the equations giving $E_0^{(0)}$, $E_0^{(1)}$ and $E_0^{(2)}$?"

Rayleigh-Schrödinger perturbation theory (Part 1)

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Gathering terms with respect to the power of λ:

$$
\begin{aligned}
\lambda^0 : &\quad \mathbf{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)} \\
\lambda^1 : &\quad \mathbf{H}^{(0)}\Psi_0^{(1)} + \mathbf{H}^{(1)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)} \\
\lambda^2 : &\quad \mathbf{H}^{(0)}\Psi_0^{(2)} + \mathbf{H}^{(1)}\Psi_0^{(1)} = E_0^{(0)}\Psi_0^{(2)} + E_0^{(1)}\Psi_0^{(1)} + E_0^{(2)} \\
\lambda^3 : &\quad \mathbf{H}^{(0)}\Psi_0^{(3)} + \mathbf{H}^{(1)}\Psi_0^{(2)} = E_0^{(0)}\Psi_0^{(3)} + E_0^{(1)}\Psi_0^{(2)} + E_0^{(2)}\Psi_0^{(1)} + E_0^{(3)}
\end{aligned}
$$

Using the intermediate normalization, we have

$$
\begin{aligned}
\lambda^0 : &\quad E_0^{(0)} = \langle \Psi_0^{(0)} | \mathbf{H}^{(0)} | \Psi_0^{(0)} \rangle \\
\lambda^1 : &\quad E_0^{(1)} = \langle \Psi_0^{(0)} | \mathbf{H}^{(1)} | \Psi_0^{(0)} \rangle \\
\lambda^2 : &\quad E_0^{(2)} = \langle \Psi_0^{(0)} | \mathbf{H}^{(1)} | \Psi_0^{(1)} \rangle \qquad \text{Wigner's (2n+1) rule!} \\
\lambda^3 : &\quad E_0^{(3)} = \langle \Psi_0^{(0)} | \mathbf{H}^{(1)} | \Psi_0^{(2)} \rangle = \langle \Psi_0^{(1)} | \mathbf{H}^{(1)} - E_0^{(1)} | \Psi_0^{(1)} \rangle
\end{aligned}
$$