Convergence Issues of Møller-Plesset Perturbation Theory in Helium-like Atoms

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Outline

- The Hartree-Fock approximation and Møller-Plesset perturbation theory
- The Delta-function model for Helium-like atoms
- The physical model for Helium-like atoms

The Ground Electonic State and the Hartree-Fock Approximation

Goal: The electronic ground state of a system of two electrons and a single nucleus of charge $Z > 0$ located at the origin:

$$H = -\frac{1}{2}\left(\Delta_{x_1} + \Delta_{x_2}\right) - Z\left(\frac{1}{|x_1|} + \frac{1}{|x_2|}\right) + \frac{1}{|x_1 - x_2|},$$

where $x_1,\, x_2 \in \mathbb{R}^3$ are the electron space coordinates.

Variational principle: $E = \min\limits_{\substack{\Psi \in D(H) \\ ||\Psi||=1}} \langle \Psi, H\Psi \rangle$.

The Hartree-Fock Approximation: Minimize over all *Slater Determinants* to obtain an upper bound $E_{HF} \geq E$.

Min. of $\langle \Psi, H\Psi \rangle$ over Slater Determinants $\Rightarrow$ Hartree-Fock equations. For $N < \sum_j Z_j + 1$ ($1 < Z$ here) minimizing solutions exist [Lieb/Simon 1977].

MP-theory: Use minimizer Ψ_0 from HF equations to construct an approximate Hamiltonian H_0 satisfying $H_0\Psi_0 = E_0\Psi_0$ (ground).

Let $V = H - H_0$ and $H(\lambda) = H_0 + \lambda V$ then use perturbation theory to find $E(\lambda),\ \Psi(\lambda)$.

Ultimately, we seek $E(1)$ and $\Psi(1)$ since $H(1) = H$.

Q: Do the series $E(\lambda)$ and $\Psi(\lambda)$ converge at $\lambda = 1$?

Recent studies suggest that it may diverge in many cases [Olsen, et. al.(1996), Stillinger(2000), Sergeev et. al.(2005)]

Departing from HF with the ground state of H_0, $H(\lambda) = H_0 + \lambda V$:

$$
\begin{aligned}
H(\lambda) \; &= \; -\frac{1}{2}\left(\Delta_{x_1} + \Delta_{x_2}\right) - Z\left(\frac{1}{|x_1|} + \frac{1}{|x_2|}\right) + \nu^{HF}_{x_1} + \nu^{HF}_{x_2} \\
&\quad + \lambda\left(\frac{1}{|x_1 - x_2|} - \left(\nu^{HF}_{x_1} + \nu^{HF}_{x_2}\right)\right)
\end{aligned}
$$

Is $E(\lambda)$ from pert. theory analytic on $\{\, \lambda \in \mathbb{C} \,|\, |\lambda| \le 1 \,\}$?

Analytic Family (Kato) $\Rightarrow$ $E(\lambda)$ is analytic in a neighborhood of $\lambda = 0$. Furthermore, it is analytic as long as it remains isolated in $\sigma(H(\lambda))$.

We look for possible $\lambda_0 \in \mathbb{R}$ at which $E(\lambda)$ runs into the bottom of $\sigma_{ess}(H(\lambda))$.

HVZ theorem: $\sigma_{ess}(H(\lambda)) = [\Sigma(\lambda), \infty)$, $-\infty < \Sigma(\lambda) \le 0$, where $\Sigma(\lambda)$ is determined by the bottom of the spectrum of non-interacting cluster decompositions:

$$H_{SI}(\lambda) \;=\; -\frac{1}{2}\Delta - \frac{Z}{|x|} + (1-\lambda)\,\nu_x^{HF}$$

$$H_{ee}(\lambda) \;=\; -\Delta + \frac{\lambda}{|x|}$$

$H_{SI}(\lambda)$ represents a bound state between the nucleus and one electron ("singly ionized" Hamiltonian).

$H_{ee}(\lambda)$ represents a bound state between the two electrons (with c.o.m. removal), infinitely separted from the nucleus ("electron-electron bound state").

Let's investigate a simplified model where many quantities are exactly solvable.

The delta-function model for a Helium-like atom

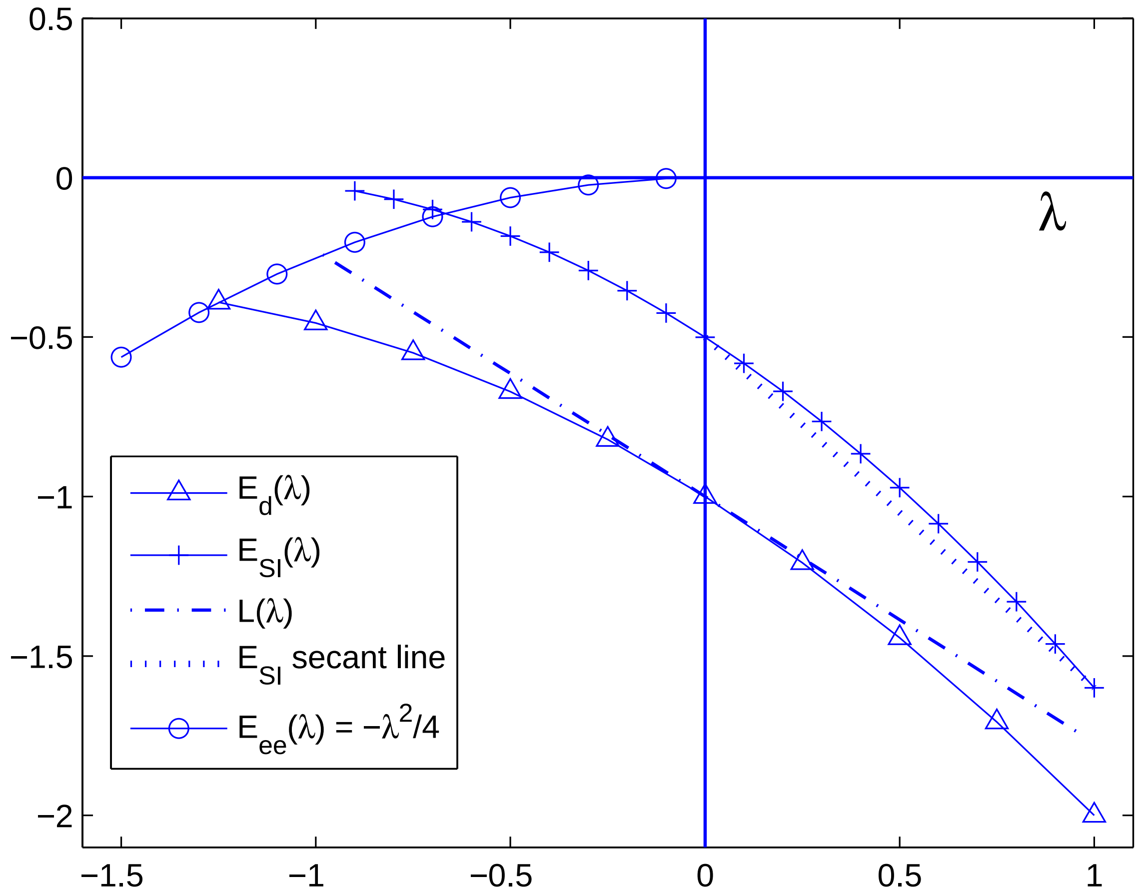
Consider the analogous Helium-like model in 1 space dimension and use delta functions in place of coulomb potentials:

$$H_D = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - Z\left(\delta(x_1) + \delta(x_2)\right) + \delta(x_1 - x_2),$$

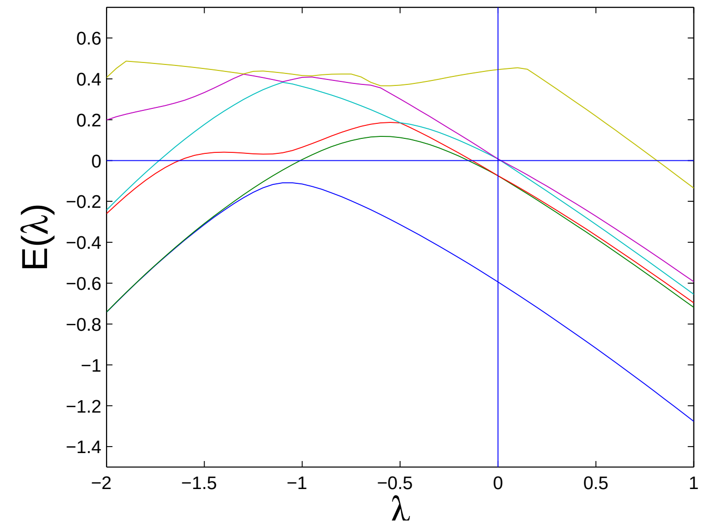
The HF equation is exactly solvable for $Z > 1/2$ [Y. Nogami, M. Vallières, and W. van Dijk, Am. J. Phys. **44**, 886 (1976).]

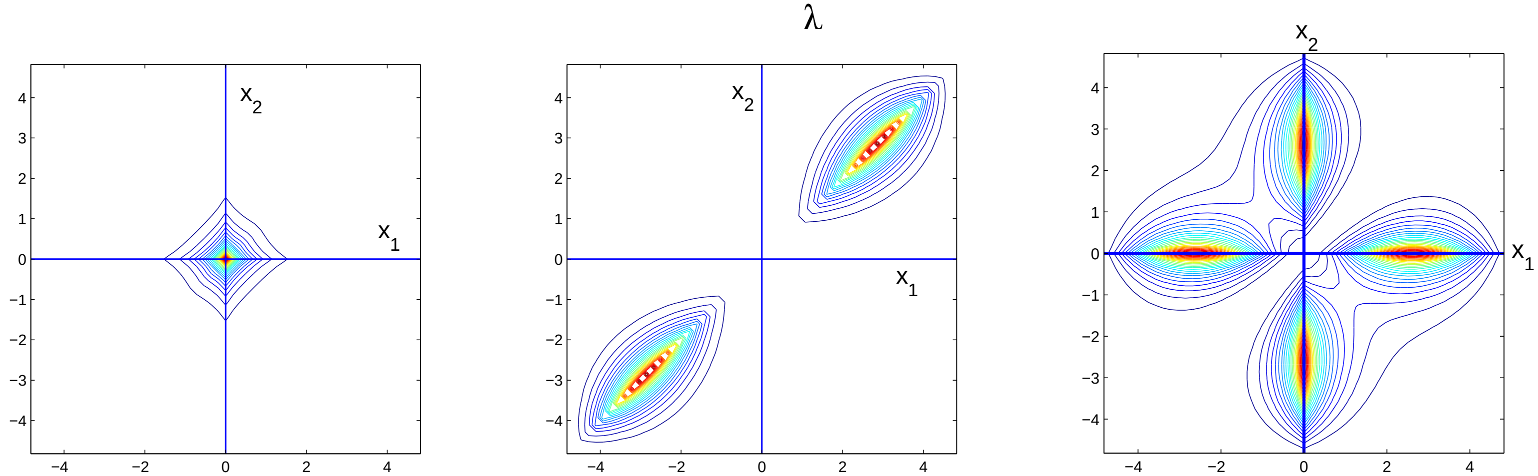
Theorem: If $Z > \frac{3}{4} + \frac{\sqrt{57}}{12} \approx 1.38$, then $E_d(\lambda) < \Sigma(\lambda)$ for $-1 \leq \lambda \leq 1$. In particular, $E_d(\lambda)$ remains an isolated point of the spectrum of $H_d(\lambda)$ for $-1 \leq \lambda \leq 1$.

Sketch of eigenvalue and thresholds



Finite Diff. ($Z = 1.38$): $\sigma_{ess}(H_d(\lambda))$ appears as clusters of eigenvalues.





Left to right: lowest state at $\lambda = -0.5$, lowest state at $\lambda = -1.85$, second state at $\lambda = 0$

The physical model

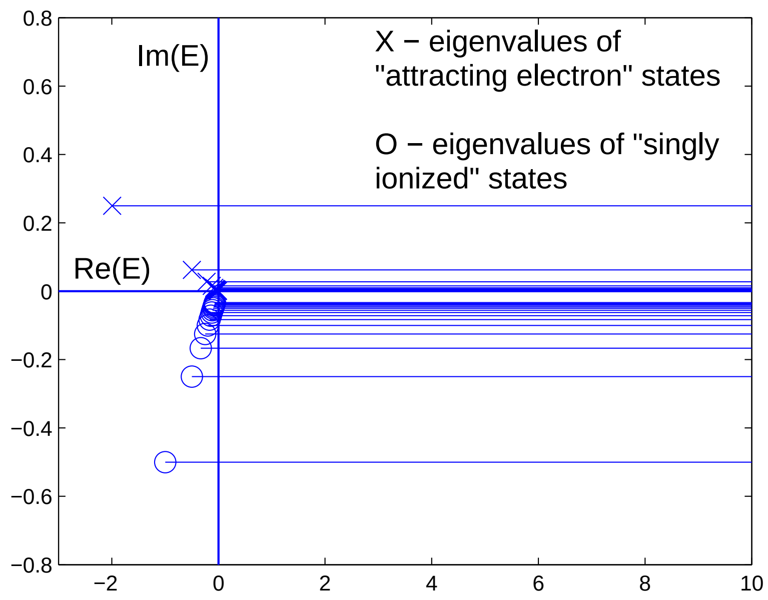
In the usual three-dimensional model, we proved an analgous result:

Theorem: If $Z > \frac{1}{16}\left(15 + \sqrt{214}\right) \approx 1.852$, then $E(\lambda) < \Sigma(\lambda)$ for $-1 \leq \lambda \leq 1$. In particular, $E(\lambda)$ remains an isolated point of the spectrum of $H(\lambda)$ for $-1 \leq \lambda \leq 1$.

The proof uses similar ideas but is more difficult since we do not have an expression for the HF solution as before.

What if Im$(\lambda) \neq 0$?

A sketch of the structure of $\sigma_{ess}(H(\lambda))$ for Im$\lambda \neq 0$:



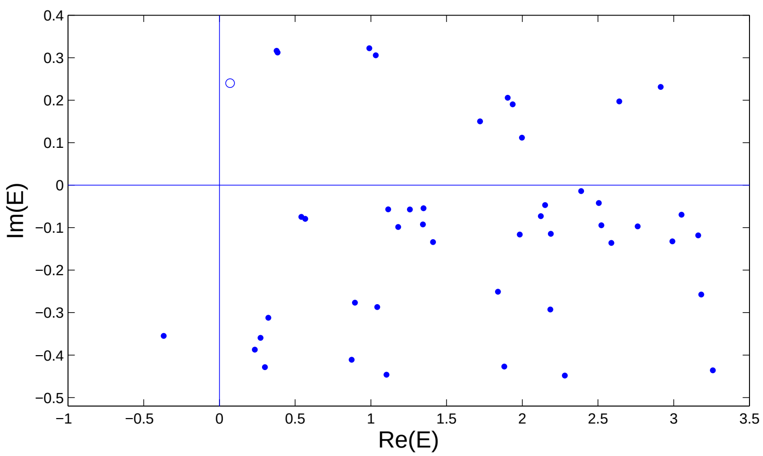
Each eigenvalue of $H_{SI}(\lambda)$ and $H_{ee}(\lambda)$ contributes a half-line of the form

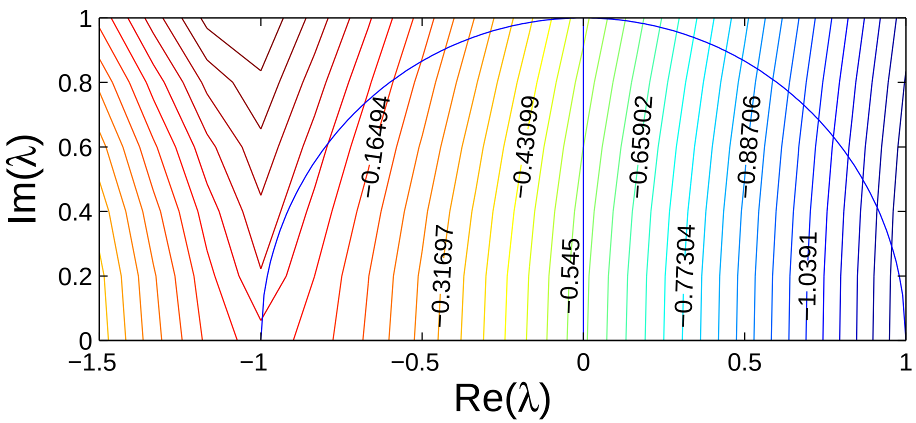
$$\{z \in \mathbb{C} \mid \text{Im}(z) = \text{Im}(E(\lambda)) \text{ and } \text{Re}(z) \geq \text{Re}(E(\lambda))\}$$

Numerical results for Im$(\lambda) \neq 0$ and $Z = 1.38$

On the left: The 45 eigenvalues with smallest real part of $H_d(\lambda)$ at $\lambda = -0.6 + 0.8i$. The ‘o’ is $\frac{-\lambda^2}{4}$ which is the exact value of $E_{ee}(\lambda)$.

On the right: contour plot in the complex plane of λ, of the real part of the eigenvalue of $H_d(\lambda)$ with smallest real part.





Conclusions

- For $\lambda \in \mathbb{R}$, the “back–door intruder,” (*i.e.,* the $E_{ee}(\lambda)$ threshold) does not cause divergence in the MP–series of the Helium atom.

- If Im$(\lambda) \neq 0$, the possibility of a collision with essential spectrum, or possible level crossings with excited states, have not been excluded.

- Numerical results from the delta model suggest that the ground state eigenvalue remains well separated from the essential spectrum for λ in the unit disk on the complex plane.