Does Møller–Plesset Perturbation Theory Converge? A Look at Two-Electron Systems

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ABSTRACT: We study the convergence or divergence of the Møller–Plesset Perturbation series for systems with two electrons and a single nucleus of charge $Z > 0$. This question is essentially to determine if the radius of convergence of a power series in the complex perturbation parameter λ is greater than 1. The power series is centered at $\lambda = 0$, so we try to find whether or not the singularity closest to $\lambda = 0$ is inside the closed unit disk in the complex plane. We give a description of possible causes for divergence in the general problem and then examine two Helium-like models. The first model is a simple one-dimensional model with delta functions in place of Coulomb potentials. The second is the realistic three-dimensional model. For each model, we show rigorously that if the nuclear charge Z is sufficiently large, there are no singularities for real values of λ between -1 and 1. Using a finite difference scheme, we present numerical results for the delta function model. The numerics are consistent with proven results and also suggest that the closest singularity occurs where λ is real and negative. Int J Quantum Chem 109: 210–225, 2009

Key words: Møller–Plesset pertusbotion theory; two-electron atoms; Hartree–Fock approximation; back door intruder state; radius of convergence

1. Introduction

Møller–Plesset (MP) perturbation theory [1] is a commonly used technique to obtain corrections to the Hartree–Fock energy for an atom or molecule. The Hartree–Fock ground state is an eigenfunction of a specific Hamiltonian H_0 that is the sum of one-electron Fock operators. H_0 is not the physical Hamiltonian of interest H_{phys}. If we define $V = H_{\text{phys}} - H_0$, then MP theory is the application of perturbation theory to the operator $H(\lambda) = H_0 + \lambda V$, to approximate the eigenvalue $E(1)$ of $H(1) = H_{\text{phys}}$. The question of convergence or divergence is to determine whether or not the radii of convergence of the power series expansions of the ground state eigenvalue $E(\lambda) = \sum_{k=0}^{\infty} E_k \lambda^k$ and ground state eigenfunction $\Psi(\lambda) = \sum_{k=0}^{\infty} \Psi_k \lambda^k$ of $H(\lambda)$ are greater than one.

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Although MP theory was developed many years ago, because of computational barriers, the question of possible divergence of the MP series has only recently been studied. Advances in technology have allowed for the computation of high-order terms in the MP series. Using a variety of basis sets, Knowles et al. [2, 3] computed MP energies up to as much as 48th order for a variety of molecules. They concluded that the series were likely converging, but slowly or erratically in some cases. More recently, several instances of divergent behavior have been observed [4–8]. Olsen and collaborators [4–6] discovered divergent behavior in MP series for several molecules and basis sets. They concluded that the divergence was the result of a "back door intruder," that is, a crossing involving the eigenvalue $E(\lambda)$ with a nonphysical excited state at some λ_0 with $\mathrm{Re}(\lambda_0) < 0$. They found the choice of basis set to be of importance in the emergence of the intruder state.

Stillinger examined this question for two–electron atoms of nuclear charge $Z > 0$ [9]. He proposed that the eigenvalue $E(\lambda)$ is an analytic function of λ in a neighborhood of the origin, but that there exists a critical point λ_c located on the negative real axis. The critical point λ_c is a singularity of $E(\lambda)$, and if $\lambda \leq \lambda_c$, then $E(\lambda)$ no longer exists as a bound state eigenvalue of $H(\lambda)$. Furthermore, λ_c corresponds to a threshold at which the molecule can be thought to dissociate into an "electron–electron bound state" running away from the nucleus. Clearly, if $\lambda_c > -1$, this phenomenon would cause divergence of the MP series. The "electron–electron bound state" is the bottom of the continuous spectrum of $H(\lambda)$, and the critical point λ_c is a threshold at which $E(\lambda)$ is absorbed into the continuous spectrum. In Section 2 we provide more detail regarding the structure of the spectrum of $H(\lambda)$. We note that contrary to [10], we see no obvious way to prove rigorously that such a critical point always exists in general. It is conceivable that the structure of ν^{HF} (to be defined in Section 2) would allow an eigenvalue to stay below this threshold for all $\lambda < 0$.

Sergeev, Goodson et al. [8, 10–12] have further analyzed this problem within the context of finite basis sets. They explained the connection between the "back door intruder" state found by Olsen and the critical point predicted by Stillinger. Once a finite basis set is chosen, one is no longer working with $H(\lambda)$, but rather an approximate Hamiltonian $H_{\mathrm{ap}}(\lambda)$. The operator $H_{\mathrm{ap}}(\lambda)$ is a matrix and has no continuous spectrum. Continuous spectrum of $H(\lambda)$ will be represented by closely clustered eigenvalues of $H_{\mathrm{ap}}(\lambda)$. So the critical point λ_c at which $E(\lambda)$ hits the continuous spectrum of $H(\lambda)$ is represented by a crossing between $E_{\mathrm{ap}}(\lambda)$ (the eigenvalue of $H_{\mathrm{ap}}(\lambda)$ that approximates $E(\lambda)$) and another eigenvalue of $H_{\mathrm{ap}}(\lambda)$. So it is possible that the "back door intruder" seen by Olsen actually corresponds to a continuum state of $H(\lambda)$, but is represented by an eigenvalue of $H_{\mathrm{ap}}(\lambda)$. An analysis of several molecules [8] concluded that basis sets that did not include diffuse functions could not model this dissociation phenomenon and as a result no critical point was found in this case. Even standard basis sets that included diffuse functions could not model the "electron–electron bound state." However, a critical point corresponding to complete dissociation of all valence electrons was found when diffuse functions were included. Upon analyzing the Ar atom, a critical point corresponding to ionization of one electron appeared to be present at some λ_c with $\mathrm{Re}(\lambda_c) > 0$ (a "front door intruder").

It is of interest to study the divergence question for the exact Hamiltonian $H(\lambda)$. We presume that the better a basis set approximates the space, the more the spectrum of $H_{\mathrm{ap}}(\lambda)$ will resemble that of the exact Hamiltonian $H(\lambda)$. We believe a rigorous mathematical description of this problem would be useful in understanding the scope of the divergence question. We first give a mathematical description of all possibilities that could cause divergence in the MP series in Section 2 and then concentrate on two-electron systems with a single nucleus of charge $Z > 0$. We present numerical results for a simplified one-dimensional model with delta functions in place of Coulomb potentials and then move to the physical model. In both models we rigorously prove lower bounds on Z for which the Stillinger critical point does not cause divergence. In particular, for a two-electron atom with nuclear charge Z, the Stillinger critical point does not cause divergence if $Z > 1.852$.

Since we first became interested in this topic, we have learned of various proposals to modify the perturbation theory to obtain convergence in certain situations. See, e.g., [13–16] and the papers referenced therein. We note that successfulness of these proposals has been only been assessed by numerical computations for specific systems in finite basis sets.

2. Possibilities for Divergence

Consider the Hamiltonian of a molecule of N electrons with positions x_i moving in a field of M nuclei with fixed positions R_j and charges $Z_j > 0$:

$$H_{\text{phys}} = -\frac{1}{2}\sum_{i=1}^{N}\Delta_{x_i} - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_j}{|x_i - R_j|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|x_i - x_j|}$$

We assume we know the Hartree–Fock wave function Ψ_0, a Slater determinant constructed from known one-electron functions $\{u_i\}_{i=1}^N$. We then construct the Hartree–Fock potential v^{HF} and Fock operator F:

$$\begin{aligned} v_i^{\text{HF}}\phi(x_i) &= \sum_{j=1}^{N}\left[\left(\int\frac{|u_j(y)|^2}{|x_i - y|}dy\right)\phi(x_i)\right. \\ &\quad \left. - \left(\int\frac{\overline{u_j(y)}}{|x_i - y|}\phi(y)dy\right)u_j(x_i)\right], \\ F_i\phi(x_i) &= -\frac{1}{2}\Delta_{x_i}\phi(x_i) - \sum_{j=1}^{M}\frac{Z_j}{|x_i - R_j|}\phi(x_i) \\ &\quad + v_i^{\text{HF}}\phi(x_i). \end{aligned} \tag{2.1}$$

Define $H_0 = \sum_{i=1}^N F_i$ and $V = H_{\text{phys}} - H_0$, and consider $H(\lambda) = H_0 + \lambda V$:

$$\begin{aligned} H(\lambda) &= -\frac{1}{2}\sum_{i=1}^{N}\Delta_{x_i} - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_j}{|x_i - R_j|} + \sum_{i=1}^{N} v_i^{\text{HF}} \\ &\quad + \lambda\left(\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|x_i - x_j|} - \sum_{i=1}^{N} v_i^{\text{HF}}\right) \end{aligned} \tag{2.2}$$

If Ψ_0 is the Hartree–Fock wave function, and ε_i are the Lagrange multipliers from the Hartree–Fock equations, then

$$H_0\Psi_0 = E_0\Psi_0, \quad \text{where} \quad E_0 = \sum_{i=1}^{N}\varepsilon_i.$$

Here E_0 and Ψ_0 are the ground state eigenvalue and eigenfunction of H_0. As described earlier, MP-theory is the use of perturbation theory to find the power series expansions $\Psi(\lambda) = \sum_{k=1}^{\infty}\Psi_k\lambda^k$ and $E(\lambda) = \sum_{k=1}^{\infty}E_k\lambda^k$ corresponding to the ground state of $H(\lambda)$, satisfying $H(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$. Since $H(1) = H_{\text{phys}}$, one uses the power series to find $E(1)$ and $\Psi(1)$. Of course, this is possible only if the radii of convergence of the series are greater than 1, or equivalently if $E(\lambda)$ is an analytic function of $\lambda \in \mathbb{C}$ for $|\lambda| \le 1$ [17].

Under specific hypotheses, analyticity of $E(\lambda)$ is guaranteed as long as $E(\lambda)$ remains an isolated point of the spectrum of $H(\lambda)$. For details see Section XII.2 of [18]. If we could show that $\text{dist}\{E(\lambda), \sigma(H(\lambda))\backslash E(\lambda)\} > 0$ for every $\lambda \in \mathbb{C}$ such that $|\lambda| \le 1$, then the power series of $E(\lambda)$ would have a radius of convergence larger than 1. Divergence can occur if either $E(\lambda)$ runs into the continuous spectrum of $H(\lambda)$ at some $|\lambda| \le 1$, or if $E(\lambda)$ is involved in a level crossing at some λ off the real axis. For details regarding the spectrum of operators, see for example [19].

We must determine the structure of the spectrum of $H(\lambda)$ for $|\lambda| \le 1$. If $\lambda \in \mathbb{R}$, $H(\lambda)$ is self-adjoint, and the well-known HVZ theorem gives us a description of the continuous spectrum. See Section XIII.5 of [18]. The continuous spectrum is determined from the spectrum of Hamiltonians of different cluster decompositions. For molecular systems with fixed nuclei, the bottom of the continuous spectrum given by the HVZ theorem corresponds to an ionization threshold. We present two examples for maximal clarity. Although they deal with specific systems, they are intended to indicate clearly how the process generalizes. We note that the usual formulation of the HVZ theorem does not actually apply here since the Hamiltonians of interest involve v^{HF}, which is not a multiplication operator in the presence of exchange terms. In Example 1 we assume that the HVZ theorem can be generalized to handle this case, although it is not obvious that it can be. This is not an issue in the proofs of Theorems 3.1 and 3.2 (below), because they do not involve exchange terms.

2.1. EXAMPLE 1

Consider a Lithium-like atom with a nucleus of charge $Z > 0$ located at the origin. Then (2.2) becomes

$$\begin{aligned} H(\lambda) &= -\frac{1}{2}\sum_{i=1}^{3}\Delta_{x_i} - Z\sum_{i=1}^{3}\frac{1}{|x_i|} + \sum_{i=1}^{3} v_i^{\text{HF}} \\ &\quad + \lambda\left(\frac{1}{|x_1 - x_2|} + \frac{1}{|x_1 - x_3|} + \frac{1}{|x_2 - x_3|} - \sum_{i=1}^{3} v_i^{\text{HF}}\right). \end{aligned}$$

To find the continuous spectrum of $H(\lambda)$, we look at the following Hamiltonians of cluster decompositions:

> $\mathbf{D_1} = \{\mathbf{Z12}\}\{\mathbf{3}\}$: The system with x_3 located a large distance from the origin, while x_1 and x_2 are near the origin. We consider

$$H_{D_1}(\lambda) = -\frac{1}{2}\sum_{i=1}^{2}\Delta_{x_i} - Z\sum_{i=1}^{2}\frac{1}{|x_i|}$$

$$+\sum_{i=1}^{2} v_i^{\mathrm{HF}} + \lambda\left(\frac{1}{|x_1 - x_2|} - \sum_{i=1}^{2} v_i^{\mathrm{HF}}\right).$$

$\mathbf{D_2} = \{\mathbf{Z1}\}\{\mathbf{23}\}$: The system with x_2 and x_3 located a large distance from the origin, but near each other, while x_1 is located near the origin. We consider

$$H_{D_2}(\lambda) = \left(-\frac{1}{2}\Delta_{x_1} - Z\frac{1}{|x_1|} + v_1^{\mathrm{HF}} + \lambda\big(-v_1^{\mathrm{HF}}\big)\right) + \left(-\Delta_{x'} + \frac{\lambda}{|x'|}\right),$$

where $x' = x_2 - x_3$, and we have removed the center of mass of the $\{2, 3\}$ cluster.
$\mathbf{D_3} = \{\mathbf{Z1}\}\{\mathbf{2}\}\{\mathbf{3}\}$: The system with x_2 and x_3 located a large distance from the origin and a large distance from each other, while x_1 is located near the origin. We consider

$$H_{D_3}(\lambda) = -\frac{1}{2}\Delta_{x_1} - Z\frac{1}{|x_1|} + v_1^{\mathrm{HF}} + \lambda\big(-v_1^{\mathrm{HF}}\big).$$

$\mathbf{D_4} = \{\mathbf{Z}\}\{\mathbf{1}\}\{\mathbf{23}\}$: The system with x_2 and x_3 located a large distance from the origin, but near each other, while x_1 is located a large distance from the origin, x_2, and x_3. We consider

$$H_{D_4}(\lambda) = -\Delta_{x'} + \frac{\lambda}{|x'|},$$

where $x' = x_2 - x_3$, and again we have removed the center of mass of the $\{2, 3\}$ cluster.
$\mathbf{D_5} = \{\mathbf{Z}\}\{\mathbf{123}\}$: The system with x_1, x_2, and x_3 located a large distance from the origin, but near each other. We consider

$$H_{D_5}(\lambda) = -\Delta_{x'} - \frac{3}{4}\Delta_{x''} + \lambda\left(\frac{1}{|x'|} + \frac{1}{|x'' - \frac{1}{2}x'|} + \frac{1}{|x'' + \frac{1}{2}x'|}\right),$$

where $x' = x_2 - x_3$, $x'' = x_1 - \frac{x_2 + x_3}{2}$, and we have removed the center of mass of the $\{1, 2, 3\}$ cluster.
$\mathbf{D_6} = \{\mathbf{Z}\}\{\mathbf{1}\}\{\mathbf{2}\}\{\mathbf{3}\}$: The system with x_1, x_2, and x_3 located a large distance from the origin and a large distance apart. This cluster decomposition contributes the half-line $[0, \infty)$ to the continuous spectrum of $H(\lambda)$.

For fixed $\lambda \in \mathbb{R}$, the HVZ theorem says that if E_{D_k} is an eigenvalue of $H_{D_k}(\lambda)$, then the half-line $\{E_{D_k} + t : t \geq 0\}$ is in the continuous spectrum of $H(\lambda)$. The continuous spectrum of $H(\lambda)$ is

$$\sigma_{\mathrm{c}}(H(\lambda)) = [0, \infty) \bigcup_{k=1}^{5} \{E_{D_k} + t : E_{D_k} \text{ is an eigenvalue of } H_{D_k}(\lambda), t \geq 0\}. \quad (2.3)$$

Since $H(\lambda)$ and the H_{D_k} are self-adjoint when $\lambda \in \mathbb{R}$, they have real eigenvalues. So the half-lines $\{E_{D_k} + t : t \geq 0\}$ are overlapping, and (2.3) can be written

$$\sigma_{\mathrm{c}}(H(\lambda)) = [\Sigma(\lambda), \infty), \quad \text{where } \Sigma(\lambda) = \min_k [\inf \sigma(H_{D_k}(\lambda))]. \quad (2.4)$$

We note that if $\lambda \geq 0$, the D_2, D_4, and D_5 cluster decompositions will not determine $\sigma_{\mathrm{c}}(H(\lambda))$. But if $\lambda < 0$, $H_{D_2}(\lambda)$, $H_{D_4}(\lambda)$ and $H_{D_5}(\lambda)$ very well could have eigenvalues below their continuous spectra, so these decompositions can determine $\sigma_{\mathrm{c}}(H(\lambda))$ in this case. It is apparent that clusters that involve only electron coordinates must also be considered in determining the continuous spectrum of $H(\lambda)$. This is the origin of the critical point predicted by Stillinger [9]. This is a consequence of the HVZ theorem and purely a mathematical issue.

Although $H(\lambda)$ is clearly not self-adjoint if λ has nonzero imaginary part, the HVZ theorem is generalized to the case where $\mathrm{Im}(\lambda) \neq 0$ by Proposition 2 of Section XIII.10 of [18]. In this case the continuous spectrum of $H(\lambda)$ still takes the form of (2.3)

$$\sigma_{\mathrm{c}}(H(\lambda)) = [0, \infty) \bigcup_{k=1}^{5} \{E_{D_k} + t : E_{D_k} \text{ is an eigenvalue of } H_{D_k}(\lambda), t \geq 0\}. \quad (2.5)$$

We provide a second example illustrating this.

2.2. EXAMPLE 2

Let $x, y \in \mathbb{R}^3$, and

$$H_0 = -\frac{1}{2}(\Delta_x + \Delta_y) - \left(\frac{1}{|x|} + \frac{1}{|y|}\right) \quad \text{and} \quad V = -\left(\frac{1}{|x|} + \frac{1}{|y|}\right),$$

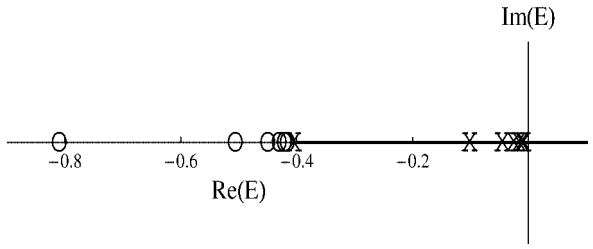

FIGURE 1. The spectrum of $H(\lambda)$ in example 2, for $\lambda = -\frac{1}{10}$. The "O" are the eigenvalues of $H(\lambda)$ that accumulate at the lowest of the eigenvalues of $-\frac{1}{2}\Delta_x - (1+\lambda)\frac{1}{|x|}$ which are labeled "X". The lowest "X" is the bottom of the continuous spectrum, which is the filled half-line on the real axis.

and consider the Hamiltonian

$$H(\lambda) = H_0 + \lambda V = -\frac{1}{2}(\Delta_x + \Delta_y) - (1+\lambda)\left(\frac{1}{|x|} + \frac{1}{|y|}\right).$$

From the well-known eigenfunctions of the Hydrogen atom Hamiltonian, we can find the eigenfunctions of $-\frac{1}{2}\Delta_x - (1+\lambda)\frac{1}{|x|}$ in terms of λ. The eigenfunctions are in $L^2(\mathbb{R}^3)$ if and only if $\mathrm{Re}(\lambda) > -1$. We see that if $\mathrm{Re}(\lambda) > -1$, $-\frac{1}{2}\Delta_x - (1+\lambda)\frac{1}{|x|}$ has eigenvalues $\left\{-\frac{(1+\lambda)^2}{2n^2}\right\}_{n=1}^{\infty}$ and continuous spectrum $[0,\infty)$. So, if $\mathrm{Re}(\lambda) > -1$, $\mathrm{Im}(\lambda) = 0$, $H(\lambda)$ has eigenvalues $\left\{-\frac{(1+\lambda)^2}{2}\left(1+\frac{1}{n^2}\right)\right\}_{n=1}^{\infty}$ that are isolated from the continuous spectrum $\left[-\frac{(1+\lambda)^2}{2}, \infty\right)$. Figure 1 shows the spectrum of $H(\lambda)$ in the complex plane for $\lambda = -\frac{1}{10}$.

If $\mathrm{Re}(\lambda) > -1$, $\mathrm{Im}(\lambda) \neq 0$, then $H(\lambda)$ has eigenvalues $\left\{-\frac{(1+\lambda)^2}{2}\left(\frac{1}{m^2} + \frac{1}{n^2}\right)\right\}_{n,m=1}^{\infty}$ that are isolated from the continuous spectrum. The continuous spectrum is made up of $[0,\infty)$ and half-lines of the form $\left\{-\frac{(1+\lambda)^2}{2n^2} + t : t \geq 0\right\}$, for $n \in \mathbb{N}$. Figure 2 shows the spectrum of $H(\lambda)$ in the complex plane for $\lambda = -\frac{1}{10} - \frac{1}{2}i$.

If $\mathrm{Re}(\lambda) \leq -1$, no eigenvalues exist and $H(\lambda)$ has only continuous spectrum of $[0,\infty)$. We note that the eigenvalues approach the continuous spectrum as $\mathrm{Re}(\lambda)$ approaches -1. We also note that the power series centered at $\lambda = 0$ representing the eigenvalues, are power 2 polynomials and have a radius of convergence of ∞. The eigenvalues approach the continuous spectrum near $\mathrm{Re}(\lambda) = -1$ and no longer exist past $\mathrm{Re}(\lambda) = -1$, but this does not cause a singularity in the functions that represent the eigenvalues when they exist. We expect that a collision between the eigenvalue and the continuous spectrum usually does cause a singularity in the eigenvalue, but showing such a collision occurs is not sufficient to prove that a singularity exits.

This example should be illustrative of the complexity of this problem. When $\mathrm{Im}(\lambda) \neq 0$, each eigenvalue of a given cluster Hamiltonian contributes a half-line to the continuous spectrum of $H(\lambda)$. In principle this could allow for infinitely many half-lines to be considered as possible culprits causing divergence in the MP series. We already mentioned that in practice the divergence issue has been found to be basis set dependent. In the absence of any general theorem regarding divergence/convergence of the MP series, this implies that divergence must be considered on a case-by-case basis. Even in small molecules this would likely make it impractical to consider continuum thresholds of each cluster decomposition individually. There has been much work devoted to classifying and approximating the location of the singularities of $E(\lambda)$ based on the terms of the MP series [10–12]. This appears much more practical.

3. Rigorous Results for Real λ

3.1. THE DELTA FUNCTION MODEL

We now concentrate on Helium-like systems with a nucleus of charge $Z > 0$ located at the origin. We first look at a simplified one-dimensional model with

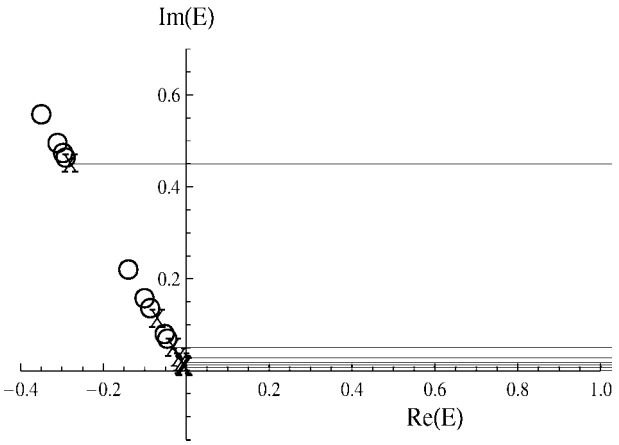

FIGURE 2. The spectrum of $H(\lambda)$ in example 2, for $\lambda = -\frac{1}{10} - \frac{1}{2}i$. The "O" are the eigenvalues of $H(\lambda)$ that accumulate at the eigenvalues of $-\frac{1}{2}\Delta_x - (1+\lambda)\frac{1}{|x|}$ labeled "X." Furthermore, these values "X" are left-endpoints of half-lines that make up $\sigma_c(H(\lambda))$.

delta functions in place of Coulomb potentials. This model will provide insight into the physical model we analyze later. Aside from the fact that many of the quantities of interest are exactly solvable in the delta function model, numerics are easily obtainable since it is one-dimensional.

The Hamiltonian of the system is

$$H_D = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - Z(\delta(x_1)+\delta(x_2)) + \delta(x_1 - x_2), \tag{3.1}$$

where x_1 and x_2 are the electron space coordinates (one-dimensional) and Z is the nuclear charge.

The restricted Hartree–Fock wave function $\Psi_d(0)$ can be written as a product,

$$\Psi_d(0)(x_1, x_2) = \phi_0(x_1)\phi_0(x_2), \tag{3.2}$$

and antisymmetrized by way of spin functions. The Hartree–Fock equation is

$$-\frac{1}{2}\frac{d^2}{dx^2}\phi - Z\delta(x)\phi + \phi^3 = \gamma\phi. \tag{3.3}$$

For $Z > 1/2$, (3.3) can be solved exactly with unique normalized solution [20]

$$\phi_0(x) = \frac{2Z-1}{\sqrt{4Z-1}} \frac{\exp\left(-\left(Z-\frac{1}{2}\right)|x|\right)}{1 - \frac{1}{4Z-1}\exp\left(-2\left(Z-\frac{1}{2}\right)|x|\right)}, \tag{3.4}$$

with $\gamma_0 = -\frac{1}{2}\left(Z-\frac{1}{2}\right)^2$.

In this case (2.1) becomes

$$v_i^{\mathrm{HF}} = \int |\phi_0(y)|^2 \delta(x_i - y)dy = \phi_0^2(x_i),$$

$$F_i = -\frac{1}{2}\frac{d^2}{dx_i^2} - Z\delta(x_i) + \phi_0^2(x_i). \tag{3.5}$$

From (3.3) we see that $F_i\phi_0(x_i) = \gamma_0\phi_0(x_i)$. Analogous to (2.2), we define

$$H_d(\lambda) = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - Z[\delta(x_1) + \delta(x_2)] + \phi_0^2(x_1) + \phi_0^2(x_2) + \lambda\big[\delta(x_1 - x_2) - \left(\phi_0^2(x_1) + \phi_0^2(x_2)\right)\big]. \tag{3.6}$$

We have $H_d(1) = H_D$, and from (3.2) and (3.3), $H_d(0)\Psi_d(0) = 2\gamma_0\Psi_d(0)$. That is, $E_d(0) = 2\gamma_0 = -(Z-\frac{1}{2})^2$ and $\Psi_d(0) = \phi_0(x_1)\phi_0(x_2)$ are the zeroth order ground state energy and wave function, respectively. Let $E_d(\lambda)$ and $\Psi_d(\lambda)$ be the eigenvalue and eigenfunction of $H_d(\lambda)$ that correspond to the ground state when $\lambda \in \mathbb{R}$.

As in example 1, we must examine Hamiltonians of different cluster decompositions to gain information about $\sigma_c(H_d(\lambda))$. There are only two cluster decompositions that are of concern. Define

$$H_{\mathrm{SI}}(\lambda) = -\frac{1}{2}\frac{d^2}{dx^2} - Z\delta(x) + \phi_0^2(x) + \lambda\left(-\phi_0^2(x)\right), \tag{3.7}$$

the "singly ionized" Hamiltonian representing a bound state between the nucleus and one electron. Let $x' = x_1 - x_2$, and define

$$H_{\mathrm{ee}}(\lambda) = -\frac{1}{2}\frac{\partial^2}{\partial x'^2} + \lambda\delta(x'), \tag{3.8}$$

the Hamiltonian (after center of mass removal), representing a bound state between the two electrons far from the nucleus. We refer to this as the "electron–electron bound state" Hamiltonian. We see that $H_{\mathrm{ee}}(\lambda)$ is just the Hamiltonian of a delta well potential of strength $-\lambda$, so if $\mathrm{Re}(\lambda) < 0$, it has one eigenvalue

$$E_{\mathrm{ee}}(\lambda) = -\frac{\lambda^2}{4}. \tag{3.9}$$

No eigenvalues exist if $\mathrm{Re}(\lambda) \geq 0$ [note that (3.9) is true for complex λ, not just real λ]. The value λ_c on the negative real axis for which $\lim_{\lambda\to\lambda_c}|E_d(\lambda) - E_{\mathrm{ee}}(\lambda)| = 0$, is the critical point predicted by Stillinger [9].

For now, we assume that λ is real, unless stated otherwise. Applying the HVZ theorem as in (2.4), we know the continuous spectrum is

$$\sigma_c(H_d(\lambda)) = [\Sigma(\lambda), \infty), \quad \text{where}$$
$$\Sigma(\lambda) = \min\{0, \inf\sigma(H_{\mathrm{SI}}(\lambda)),\ \inf\sigma(H_{\mathrm{ee}}(\lambda))\}. \tag{3.10}$$

Applying the HVZ Theorem to $H_{\mathrm{SI}}(\lambda)$ and $H_{\mathrm{ee}}(\lambda)$ we get

$$\sigma_c(H_{\mathrm{SI}}(\lambda)) = \sigma_c(H_{\mathrm{ee}}(\lambda)) = [0, \infty).$$

Let $E_{\mathrm{SI}}(\lambda)$ be the lowest eigenvalue of $H_{\mathrm{SI}}(\lambda)$, if any exist. Then

$$\inf\sigma(H_{\mathrm{SI}}(\lambda)) = \min\{0, E_{\mathrm{SI}}(\lambda)\}$$
$$\inf\sigma(H_{\mathrm{ee}}(\lambda)) = \min\{0, E_{\mathrm{ee}}(\lambda)\}$$

See sketch in Figure 3.

Theorem 3.1: If

$$Z > \frac{3}{4} + \frac{\sqrt{57}}{12} \approx 1.38, \tag{3.11}$$

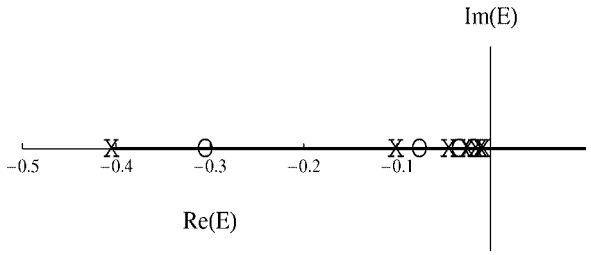

FIGURE 3. A qualitative sketch of the structure of $\sigma_c(H_d(\lambda))$ at some $\lambda \in \mathbb{R}$ and some $Z > 0$. The "O" are the eigenvalues of $H_{SI}(\lambda)$ and the "X" are the eigenvalues of $H_{ee}(\lambda)$.

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 $-1 \leq \lambda \leq 1$.

The details of the proof are presented in the Appendix. We provide an outline here.

The proof relies heavily on the fact that $E_d''(\lambda) \leq 0$ inside the region of analyticity, which comes from perturbation formulas. It follows that the graph of $E_d(\lambda)$ lies below its tangent lines. The tangent line to $E_d(\lambda)$ at $\lambda = 0$ can be found exactly. We refer to this tangent line as $L(\lambda)$. The proof is separated into the two cases that can cause divergence, the "singly ionized" threshold $E_{SI}(\lambda)$ and the "electron–electron bound state" threshold $E_{ee}(\lambda)$:

1. We show that $L(\lambda) < E_{SI}(\lambda)$ for $0 \leq \lambda \leq 1$, provided $Z > \frac{1}{2}(1 + \frac{1}{\sqrt{3}}) \approx 0.7887$. We use $E_{SI}''(\lambda) \leq 0$ (also coming from perturbation formulas), which implies that the graph of $E_{SI}(\lambda)$ lies above its secant lines. We show that the secant line passing through $(0, E_{SI}(0))$ and $(1, E_{SI}(1))$ is above $L(\lambda)$. See sketch on Figure 4. We then use a simple argument to show $E_d(\lambda) < E_{SI}(\lambda)$, for $-1 \leq \lambda < 0$.
2. We show that $L(\lambda) < E_{ee}(\lambda)$ for $-1 \leq \lambda < 0$, provided Z is above the bound in (3.11). This is simple since we are able to obtain $L(\lambda)$ and $E_{ee}(\lambda)$ exactly. See sketch on Figure 5. From this, it easily follows that $E_d(\lambda) < 0$, ruling out the threshold at 0 as a possible issue.

Figure 6 shows a qualitative sketch of the eigenvalue and thresholds in question, along with the tangent and secant lines that are relevant to the proof.

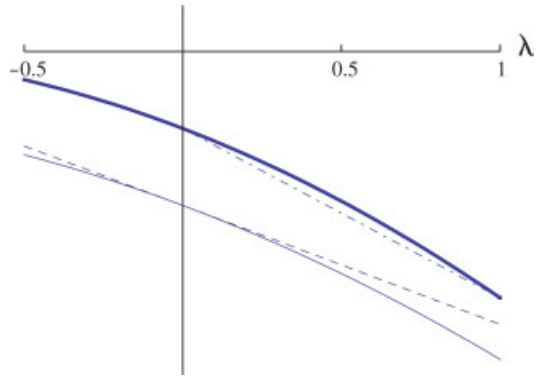

FIGURE 4. A qualitative sketch of the eigenvalue and "singly ionized" threshold in the delta model, for $-0.5 \leq \lambda \leq 1$ and some $Z > 0$. $E_d(\lambda)$ is the thin solid curve, its tangent line at $\lambda = 0$ is the dashed line, $E_{SI}(\lambda)$ is the thick curve, and the secant line through $(0, E_{SI}(0))$ and $(1, E_{SI}(1))$ is dash dotted. We show that for appropriate Z and $0 \leq \lambda \leq 1$, the graph of $E_d(\lambda)$ lies below the tangent line, the tangent line lies below the secant line, and the secant line lies below the graph of $E_{SI}(\lambda)$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

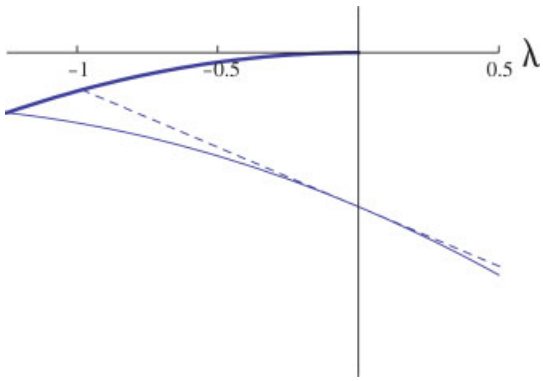

FIGURE 5. A qualitative sketch of the eigenvalue and "electron-electron bound state" threshold in the delta model, for $-1.25 \leq \lambda \leq 0.5$ and some $Z > 0$. $E_d(\lambda)$ is the thin solid curve, its tangent line at $\lambda = 0$ is the dashed line, and $E_{ee}(\lambda)$ is the thick curve. We show that for appropriate Z and $-1 \leq \lambda < 0$, the graph of $E_d(\lambda)$ lies below the tangent line and the tangent line lies below the graph of $E_{ee}(\lambda)$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3.2. THE PHYSICAL MODEL

We now turn our attention to the physical model of Helium-like atoms. The Hamiltonian of the system is

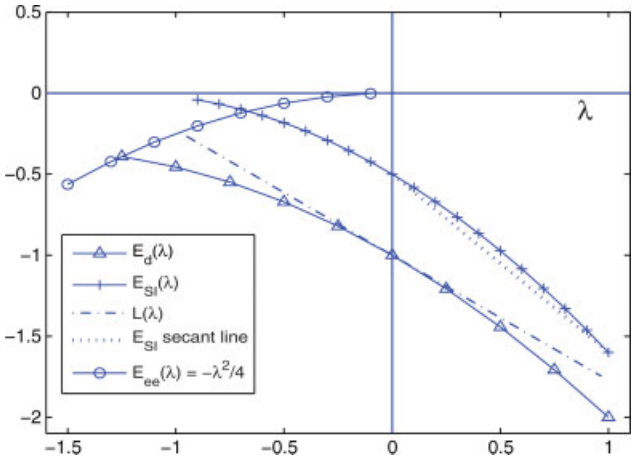

FIGURE 6. A qualitative sketch of the eigenvalue and thresholds in question in the delta model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$H_{\text{phys}} = -\frac{1}{2}(\Delta_{x_1} + \Delta_{x_2}) - Z\left(\frac{1}{|x_1|} + \frac{1}{|x_2|}\right) + \frac{1}{|x_1 - x_2|}, \tag{3.12}$$

where again x_1 and x_2 are the electron space coordinates (three-dimensional) and $Z > 0$ is the nuclear charge. As before, the restricted Hartree–Fock wave function $\Psi_{\text{ph}}(0)$ can be written as a product,

$$\Psi_{\text{ph}}(0)(x_1, x_2) = \phi_0(x_1)\,\phi_0(x_2), \tag{3.13}$$

and antisymmetrized by way of spin functions. The Hartree–Fock equation is

$$-\frac{1}{2}\Delta\phi(x) - \frac{Z}{|x|}\phi(x) + \left(\int \frac{|\phi(y)|^2}{|x-y|}dy\right)\phi(x) = \gamma\,\phi(x). \tag{3.14}$$

While the solution to (3.14) is not known explicitly, as in the delta model, it has been proved [21] that for $Z > 1$, there exists ϕ_0 with $||\phi_0|| = 1$, such that $\Psi_{\text{ph}}(0)$ from (3.13) minimizes $\langle\Psi, H_{\text{phys}}\Psi\rangle$ over all such restricted Slater determinants. In addition, ϕ_0 must solve (3.14) with eigenvalue $\gamma_0 < 0$. Define the Hartree–Fock potential v^{HF} and the Fock operator F to be

$$v_i^{\text{HF}} = \int \frac{|\phi_0(y)|^2}{|x_i - y|}dy,$$
$$F_i = -\frac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} + v_i^{\text{HF}}, \tag{3.15}$$

We have $F_i\phi_0(x_i) = \gamma_0\phi_0(x_i)$, and it has been proved [21] that $\gamma_0 = \inf\{\sigma(F_i)\}$. Again consider $H_{\text{ph}}(\lambda) = H_0 + \lambda V$ where

$$H_0 = F_1 + F_2,$$
$$V = \frac{1}{|x_1 - x_2|} - \left(v_1^{\text{HF}} + v_2^{\text{HF}}\right). \tag{3.16}$$

Analogous to the delta model, we have $H_{\text{ph}}(1) = H_0 + V = H_{\text{phys}}$, with $E_{\text{ph}}(0) = 2\gamma_0$, and $\Psi_{\text{ph}}(0)$ the zeroth order ground state energy and wave function, respectively. Let $E_{\text{ph}}(\lambda)$ and $\Psi_{\text{ph}}(\lambda)$ be the eigenvalue and eigenfunction of $H_{\text{ph}}(\lambda)$ that correspond to the ground state when $\lambda \in \mathbb{R}$. As before, we must show $\text{dist}\{E_{\text{ph}}(\lambda), \sigma_{\text{c}}(H_{\text{ph}}(\lambda))\} > 0$ if $\lambda \in \mathbb{R}$. Define the "singly ionized" and "electron–electron bound state" Hamiltonians as in (3.7) and (3.8):

$$H_{\text{SI}}(\lambda) = -\frac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} + v_i^{\text{HF}} + \lambda\left(-v_i^{\text{HF}}\right), \tag{3.17}$$

$$H_{\text{ee}}(\lambda) = -\Delta_{x'} + \frac{\lambda}{|x'|}, \tag{3.18}$$

where $x' = x_1 - x_2$. Here $H_{\text{ee}}(\lambda)$ is a hydrogenic Hamiltonian with charge $Z = -\frac{\lambda}{\sqrt{2}}$. The lowest eigenvalue is $E_{\text{ee}}(\lambda) = -\frac{\lambda^2}{4}$ if $\text{Re}(\lambda) < 0$, and no eigenvalues exist for $\text{Re}(\lambda) \geq 0$. Also, in this formulation (3.10) still holds. Note that if λ is complex, we need to consider all of the bound states of $H_{\text{ee}}(\lambda)$, namely $E_{\text{ee}}^{(n)}(\lambda) = -\frac{\lambda^2}{4n^2}$. We discuss this later.

Theorem 3.2: If

$$Z > \frac{1}{16}\left(15 + \sqrt{214}\right) \approx 1.852, \tag{3.19}$$

then $E_{\text{ph}}(\lambda) < \Sigma(\lambda)$ for $-1 \leq \lambda \leq 1$. In particular, $E_{\text{ph}}(\lambda)$ remains an isolated point of the spectrum of $H_{\text{ph}}(\lambda)$ for $-1 \leq \lambda \leq 1$.

The details of the proof are presented in the Appendix.

The proof is similar to the proof of Theorem 3.1 in the delta function model. Many of the corresponding quantities that were exactly solvable in the delta function model are no longer explicitly obtainable, but we are able rigorously to obtain (3.19) with the use of trial functions. It is apparent that the eigenvalue and thresholds behave qualitatively the same as in the delta function model, illustrated in Figure 6.

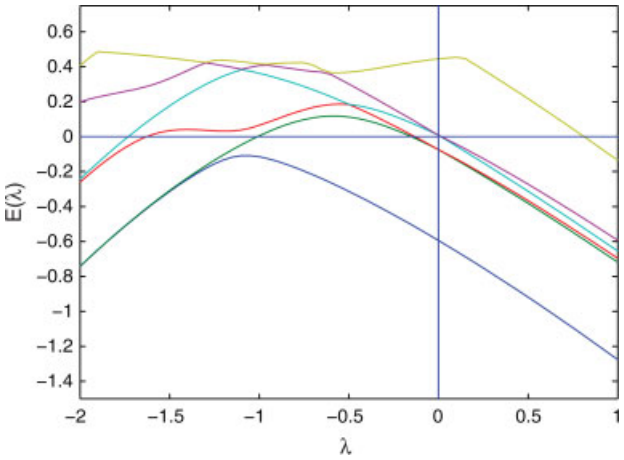

FIGURE 7. A numerical plot of the smallest six eigenvalues of $h_d(\lambda)$ on $-2 \leq \lambda \leq 1$, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

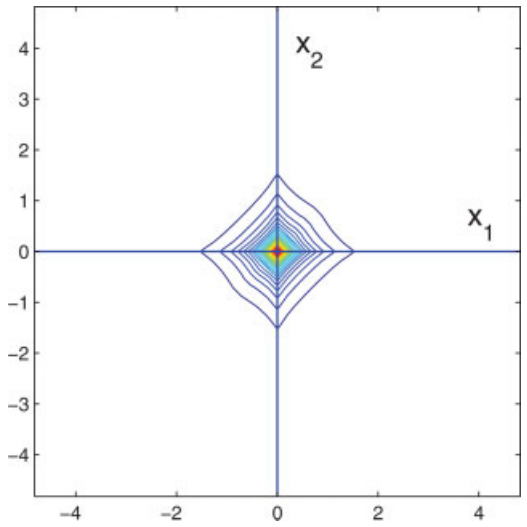

FIGURE 8. A contour plot of the eigenfunction squared corresponding to the smallest eigenvalue of $h_d(\lambda)$ at $\lambda = -0.5$, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

4. Numerical Results for the Delta Function Model for Real λ

We have numerical results for the delta model from an elementary finite difference scheme. The space is discretized into grid points, so the continuous variables x_1, x_2 have become discrete variables. The derivative operators are approximated by matrices via difference quotients. The problem is constrained to a box, with boundary conditions that require the eigenfunctions go to zero on the boundary. The Hamiltonians are all matrices, so all spectrum comes in the form of eigenvalues. Let $h_d(\lambda)$ and $h_{\mathrm{SI}}(\lambda)$ be the matrix approximations to $H_d(\lambda)$ and $H_{\mathrm{SI}}(\lambda)$, respectively. Clusters of eigenvalues of $h_d(\lambda)$ correspond to continuous spectrum $\sigma_c(H_d(\lambda))$ of the actual operator. By looking at a contour plot of an eigenvector corresponding to a specific low-lying eigenvalue of $h_d(\lambda)$, we can determine if it corresponds to a bound state eigenvalue or if it corresponds to a piece of continuous spectrum of $H_d(\lambda)$. Negative energy states corresponding to the continuous spectrum are "singly ionized states," or "electron–electron bound states." All plots shown are for $Z = 1.38$, corresponding to the value in (3.11).

For a variety of choices of λ, we computed several of the eigenvalues of $h_d(\lambda)$ with smallest real parts. Figures 8–10 show contour plots of the absolute squares of some eigenfunctions of $h_d(\lambda)$ at different values of λ. The functions are approximately zero outside the regions where the contours lie. In Figure 7, the lowest curve on approximately $-1.1 \leq \lambda \leq 1$ corresponds to $E_d(\lambda)$. To the left of about $\lambda = -1.1$ it is absorbed into the continuous spectrum of $H_d(\lambda)$. Figure 8 shows a plot of the eigenfunction squared of this lowest eigenvalue at $\lambda = -0.5$. We can see it is a bound state with the probability density near zero outside a region around the origin. This is a state with both electrons near the nucleus.

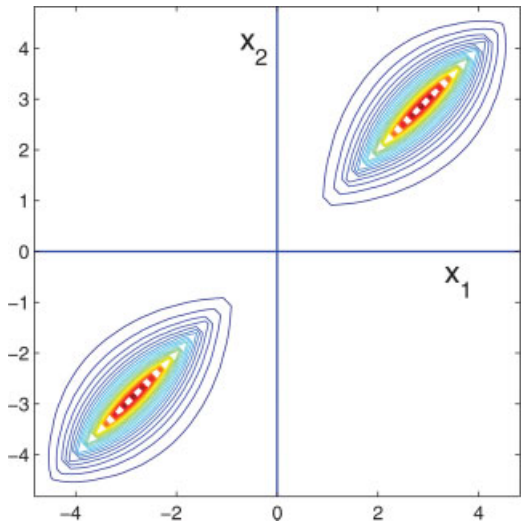

FIGURE 9. A contour plot of the eigenfunction squared corresponding to the smallest eigenvalue of $h_d(\lambda)$ at $\lambda = -1.85$, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

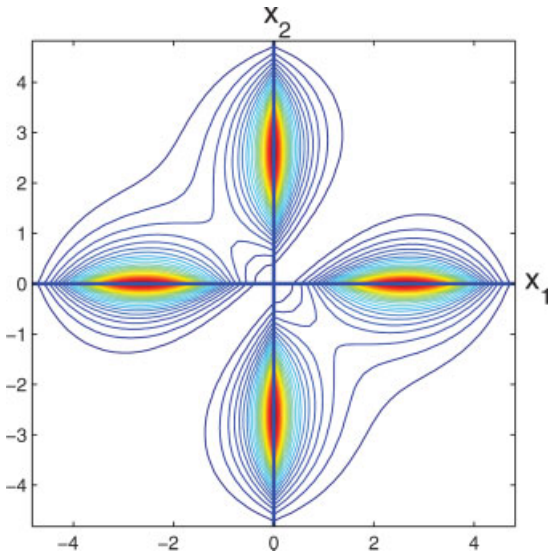

FIGURE 10. A contour plot of the eigenfunction squared corresponding to the second smallest eigenvalue of $h_d(\lambda)$ at $\lambda = 0$, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

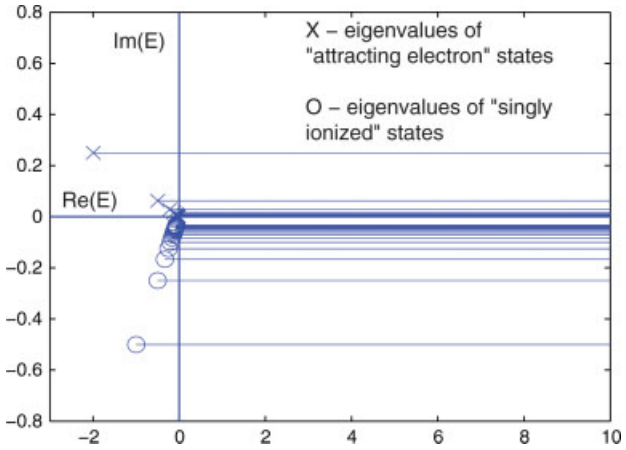

FIGURE 11. A qualitative sketch of the structure of $\sigma_c(H_{ph}(\lambda))$ at some $\lambda = \alpha + i\beta$, $\beta \neq 0$ and some $Z > 0$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The lowest curve on Figure 7 from about $-2 \leq \lambda \leq -1.1$ corresponds to $E_{ee}(\lambda)$. Figure 9 shows the eigenfunction squared of the lowest state at $\lambda = -1.85$. Notice that the probability density is near zero outside regions along $x_1 = x_2$ with x_1 and x_2 far from zero. This is a state where both electrons are near each other but away from the nucleus fixed at the origin. The second lowest eigenvalue on about $-0.3 \leq \lambda \leq 1$ corresponds to the $E_{SI}(\lambda)$ threshold. This is a "singly ionized" state. Figure 10 shows a plot of the eigenfunction squared at $\lambda = 0$. The probability density is near zero outside regions along the coordinate axes and away from the origin. This is a state where one electron is near the nucleus, while the other is far away.

5. Considering Complex λ

As mentioned earlier, we need to show $E_d(\lambda)$ is an isolated point of $\sigma(H_d(\lambda))$ for all $|\lambda| \leq 1$, so we must consider complex λ. If λ is not real, in addition to showing that $E_d(\lambda)$ stays away from $\sigma_c(H_d(\lambda))$, we must also consider the possibility of level crossings upsetting analyticity of $E_d(\lambda)$. As we already mentioned, the usual HVZ theorem is not applicable for non–self-adjoint operators but it is generalizable to handle $H_d(\lambda)$ and $H_{ph}(\lambda)$ in the case $\mathrm{Im}(\lambda) \neq 0$, taking the form of (2.5). See the sketch in Figure 11.

5.1. NUMERICAL RESULTS FOR THE DELTA FUNCTION MODEL WITH $\lambda = \alpha + i\beta$, $\beta \neq 0$

The structure of $\sigma_c(H_d(\lambda))$ for $\lambda = -0.6 + 0.8i$ can be seen in the numerical approximation in Figure 12. Notice the cluster of eigenvalues starting near $E_{ee}(\lambda)$ and running off to infinity towards the right. If we plotted the eigenvectors corresponding to these

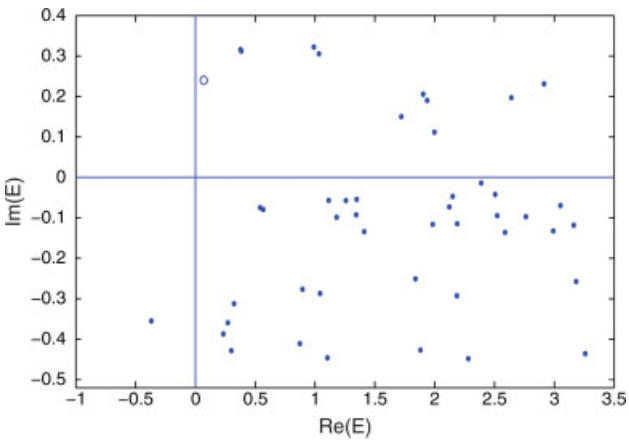

FIGURE 12. A plot of the 45 eigenvalues with smallest real part of $h_d(\lambda)$ at $\lambda = -0.6 + 0.8i$, for $Z = 1.38$. The "o" is $\frac{-\lambda^2}{4}$ which is the exact value of $E_{ee}(\lambda)$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

eigenvalues, we would see that these are "electron–electron bound states." The cluster starting near the point $0.2 - 0.4i$ corresponds to the half-line from the $E_{\mathrm{SI}}(\lambda)$ threshold. If we plotted the eigenvectors, we would see these are "singly ionized" states. The eigenvalue located near $-0.35 - 0.35i$ appears to be the one and only bound state of $h_d(\lambda)$, corresponding to $E_d(\lambda)$. Again we would see this if we plotted the eigenvector.

If there is only one bound state in the delta model at each $\lambda \in \{\lambda : |\lambda| \leq 1\}$, then level crossings are not a concern. One would only need to show that $E_d(\lambda)$ remains a positive distance from $\sigma_{\mathrm{c}}(H_d(\lambda))$ at each λ. We note that this is not true in the physical model since Helium is known to have infinitely many bound states. So in the physical model, one would need to rule out the possibility of level crossings causing a singularity in $E_{\mathrm{ph}}(\lambda)$.

Contour plots in the complex λ plane, of the real and imaginary parts of the eigenvalue of $h_d(\lambda)$ with smallest real part, are shown in Figures 13 and 14. Again we chose $Z = 1.38$. The plot is given in the upper half-plane only since we know $E_d(\overline{\lambda}) = \overline{E_d(\lambda)}$ by the Schwartz reflection principle [17]. Only the sign of the imaginary part of $E_d(\lambda)$ changes in the lower half-plane, i.e., points upsetting analyticity come in conjugate pairs. The unit circle is included in the plot since it is the region of interest. Since we know that $E_d(\lambda)$ has smallest real part on the real axis compared to the rest of $\sigma(H_d(\lambda))$ (at least for large enough λ and Z as shown earlier), the smoothness of the plots suggest that this is a plot of $E_d(\lambda)$. Furthermore it appears that $E_d(\lambda)$ is analytic and it remains away from $\sigma_{\mathrm{c}}(H_d(\lambda))$ as long as $\mathrm{Re}(\lambda) > -1$. The "noise" near $\mathrm{Re}(\lambda) = -1$ suggests either a collision

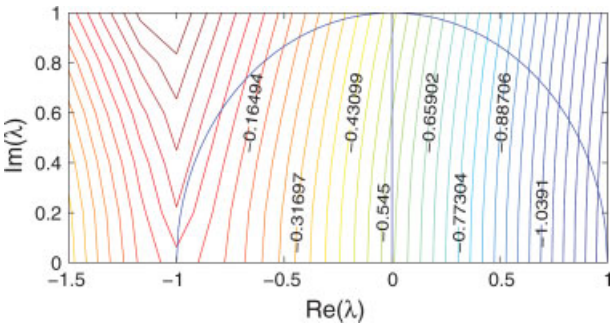

FIGURE 13. A contour plot of the real part of the eigenvalue of smallest real part of $h_d(\lambda)$ on the complex plane of λ, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

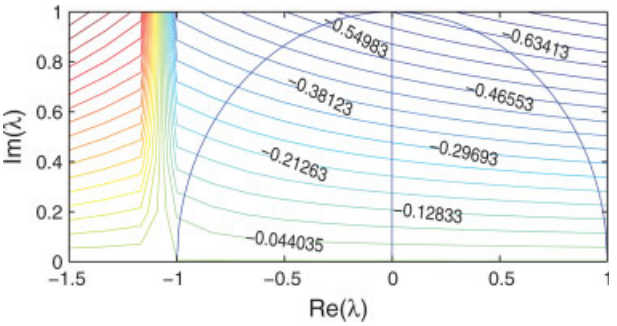

FIGURE 14. A contour plot of the imaginary part of the eigenvalue of smallest real part of $h_d(\lambda)$ on the complex plane of λ, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of $E_d(\lambda)$ with the half-line from the $E_{\mathrm{ee}}(\lambda)$ threshold (and so also a collision with $\sigma_{\mathrm{c}}(H_d(\lambda))$) or a different eigenvalue of $h_d(\lambda)$ is becoming the one with smallest real part. Recall from Figure 7, $E_d(\lambda)$ appears to collide with $\sigma_{\mathrm{c}}(H(\lambda))$ near $\lambda = -1.1$.

Let $\alpha = \mathrm{Re}(\lambda)$, $\beta = \mathrm{Im}(\lambda)$. Notice from Figure 14 that $\mathrm{Im}\,(E_d(\lambda))$ is negative and decreasing as β increases. Note that

$$\mathrm{Im}(E_d(\lambda)) = \beta \frac{\langle \Psi_d(\lambda), V\Psi_d(\lambda)\rangle}{\langle \Psi_d(\lambda), \Psi_d(\lambda)\rangle} \quad \text{implies}$$

$$\begin{aligned}\mathrm{sgn}\,\{\mathrm{Im}(E_d(\lambda))\} &= \mathrm{sgn}\,\{\beta\langle \Psi_d(\lambda), V\Psi_d(\lambda)\rangle\} \\ &= \mathrm{sgn}\,\big\{\beta\big[\big\langle \Psi_d(\lambda), \big(\delta(x_1 - x_2) - \nu_1^{\mathrm{HF}}\big)\Psi_d(\lambda)\big\rangle \\ &\qquad - \big\langle \Psi_d(\lambda), \nu_2^{\mathrm{HF}}\Psi_d(\lambda)\big\rangle\big]\big\}.\end{aligned}$$

We believe that $\langle \Psi_d(\lambda), (\delta(x_1 - x_2) - \nu_1^{\mathrm{HF}})\Psi_d(\lambda)\rangle$, which is 0 at $\lambda = 0$, remains small, and thus

$$\begin{aligned}\mathrm{sgn}\,\{\mathrm{Im}(E_d(\lambda))\} &= \mathrm{sgn}\,\big\{-\beta\big\langle \Psi_d(\lambda), \nu_2^{\mathrm{HF}}\Psi_d(\lambda)\big\rangle\big\} \\ &= -\,\mathrm{sgn}\,\{\beta\}.\end{aligned}$$

Since $\mathrm{sgn}\,\{\mathrm{Im}(E_{\mathrm{ee}}(\lambda))\} = \mathrm{sgn}\,\{-\frac{1}{2}\alpha\beta\} = \mathrm{sgn}\,\{\beta\}$ for $\alpha < 0$, it appears that $\mathrm{Im}(E_d(\lambda))$ and $\mathrm{Im}(E_{\mathrm{ee}}(\lambda))$ have opposite sign. So if $\beta \neq 0$, $E_d(\lambda)$ cannot approach the piece of $\sigma_{\mathrm{c}}(H_d(\lambda))$ coming from the $E_{\mathrm{ee}}(\lambda)$ threshold.

The plots of $\mathrm{Re}(E_{\mathrm{SI}}(\lambda))$ and $\mathrm{Im}(E_{\mathrm{SI}}(\lambda))$ given in Figures 15 and 16 show that $E_{\mathrm{SI}}(\lambda)$ exhibits behavior similar to that of $E_d(\lambda)$. Notice that the contours of $\mathrm{Re}\,(E_d(\lambda))$ and $\mathrm{Re}\,(E_{\mathrm{SI}}(\lambda))$ are nearly horizontal. The real parts change little as β increases. Since $\mathrm{Re}(E_d(\lambda))$ is lower than $\mathrm{Re}(E_{\mathrm{SI}}(\lambda))$ for $-1 \leq \lambda = \alpha \leq 1$ and appropriate nuclear charge $Z > 0$, we conclude that it remains as such for $\lambda = \alpha + i\beta$ inside the unit disk.

5.2. RELATING THE DELTA MODEL TO THE PHYSICAL MODEL

Since the structures of the delta and physical models are rather similar, it is natural to assume that $E_d(\lambda)$ in the physical model behaves much the same in relation to the pieces of $\sigma_c(H_{ph}(\lambda))$ which arise from the bound states of $H_{SI}(\lambda)$ and $H_{ee}(\lambda)$. Although there are infinitely many bound states of $H_{ee}(\lambda)$ when $\mathrm{Re}(\lambda) < 0$ in the physical model, we know them explicitly from (3.18) to be $E_{ee}^{(n)}(\lambda) = -\frac{\lambda^2}{4n^2}$. So, $\mathrm{sgn}\{\mathrm{Im}(E_{ee}^{(n)}(\lambda))\} = \mathrm{sgn}\{\beta\}$, and we expect that $\mathrm{Im}(E_{ph}(\lambda))$ and $\mathrm{Im}(E_{ee}^{(n)}(\lambda))$ probably have opposite sign inside $\{\lambda : |\lambda| \leq 1\}$ if $Z > \frac{1}{16}(15 + \sqrt{214}) \approx 1.852$. Furthermore, $\mathrm{Re}(E_{ph}(\lambda))$ and $\mathrm{Re}(E_{SI}(\lambda))$ probably change little as β increases as in the delta model. We also believe that the second derivatives of $E_{ph}(\lambda)$ and $E_{SI}(\lambda)$ are small (as suggested by Figure 7). If one could show these quantities were approximately linear, it could lead to a proof of the necessary result.

The only remaining issue would then be to remove the possibility of level crossings involving $E_{ph}(\lambda)$ with other bound states of $H_{ph}(\lambda)$ at some complex λ in the unit disk. Since only one bound state appears in the delta model, we cannot use it to obtain any insight into this problem. Do the other bound states act similarly to $E_{ph}(\lambda)$ when λ is complex? If so, we would conclude there is no crossing involving $E_{ph}(\lambda)$, and most likely it is analytic inside the unit disk.

The underlying complexity of this type of analysis is mainly due to the non-self-adjointness of the Hamiltonians when λ is not real. This makes it difficult to prove any useful properties of the bound states or thresholds. Any upper bounds on

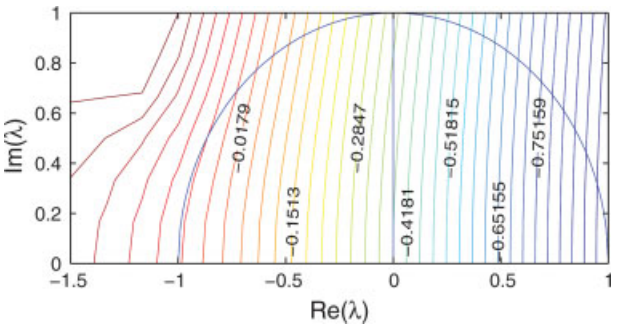

FIGURE 15. A contour plot of the real part of the eigenvalue of smallest real part of $h_{SI}(\lambda)$ in the delta model, on the complex plane of λ, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

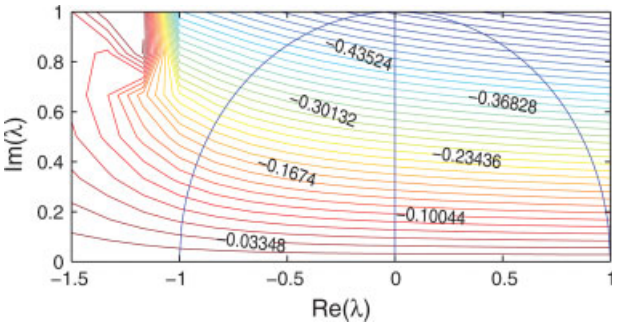

FIGURE 16. A contour plot of the imaginary part of the eigenvalue of smallest real part of $h_{SI}(\lambda)$ in the delta model, on the complex plane of λ, for $Z = 1.38$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$\mathrm{Re}(E_{ph}(\lambda))$ or $\mathrm{Im}(E_{ph}(\lambda))$ (or their derivatives for that matter) seem not easily obtainable.

It should be noted that even if there exists λ_0 with $|\lambda_0| \leq 1$ at which there is a level crossing involving $E_{ph}(\lambda)$, or where $E_{ph}(\lambda)$ is absorbed into $H_{ph}(\sigma_c(\lambda))$, it does not necessarily cause a singularity in the function $E_{ph}(\lambda)$. It may be that $E_{ph}(\lambda_0)$ is not an eigenvalue of $H_{ph}(\lambda_0)$ but $E_{ph}(\lambda)$ is analytic at $\lambda = \lambda_0$. Example 2 has a simple illustration of this possibility. The behavior of eigenvalues (with regard to analyticity) near points at which they absorb into continuous spectrum has been previously analyzed under certain hypotheses in [22] and [23].

6. Conclusion

We examined the question of Møller–Plesset convergence for Helium-like systems. Singularities in the eigenvalue cannot occur if the eigenvalue remains an isolated point of the spectrum of the perturbed Hamiltonian $H_{ph}(\lambda)$. For $\lambda \in \mathbb{R}$, one need only show that the eigenvalue remains a positive distance from the continuous spectrum of $H_{ph}(\lambda)$. The continuous spectrum can be described in terms of bound states of "ionized" Hamiltonians. As previously conjectured, there may exist a singularity in the eigenvalue at some negative value of the perturbation parameter λ, at which the eigenvalue approaches a threshold corresponding to an "electron–electron bound state." This is not the only possible occurrence of a singularity however. There may be singularities arising from this "electron–electron bound state" at

some complex λ in the left half-plane. The singly ionized state, a bound state between one electron and the nucleus, may also cause divergence. When λ is complex, it is also possible that the existence of level crossings can cause a singularity in the eigenvalue in question.

The simplified delta function model considered here gives insight into the nature of the physical problem. In the delta function model we showed that if $Z > \frac{3}{4} + \frac{\sqrt{57}}{12} \approx 1.38$, then there does not exist a singularity at any $\lambda \in \mathbb{R}$ with $-1 \leq \lambda \leq 1$. Using a similar approach, we showed the same for the physical problem if $Z > \frac{1}{16}\left(15 + \sqrt{214}\right) \approx 1.852$.

While there is not yet a proof excluding the possibility of singularities at complex values of λ inside the unit disk, the numerics provided in the delta function model are encouraging. The eigenvalue appears to move away from these thresholds as the imaginary part of λ increases. It seems apparent that there is at most one bound state for each of $H_d(\lambda), H_{\mathrm{SI}}(\lambda)$, and $H_{\mathrm{ee}}(\lambda)$ in the delta model. So level crossings are not a concern, and we only need to know the distance from the eigenvalue to two thresholds. This is dramatically simpler when compared with the physical problem where each of these Hamiltonians has infinitely many bound states. Level crossings are certainly an issue in this case and there are infinitely many pieces of $\sigma_{\mathrm{c}}(H_{\mathrm{ph}}(\lambda))$ with thresholds associated with each of the bound states of $H_{\mathrm{SI}}(\lambda)$ and $H_{\mathrm{ee}}(\lambda)$.

While this gives much insight into the nature of the convergence of Møller–Plesset for the Helium atom, this is a far cry from obtaining any sort of general result concerning atoms or molecules. Even the Lithium atom problem is much more complicated for various reasons, not the least of which is spin considerations.

APPENDIX

Here we present the details of the proofs of Theorem 1 and Theorem 2.

PROOF OF THEOREM 3.1

We first need some perturbation formulas. Let $H_d(\lambda) = H_0 + \lambda V$, where H_0 and V are defined by (3.6). Inside the region of analyticity of $E_d(\lambda)$ we have $H_d(\lambda)\Psi_d(\lambda) = E_d(\lambda)\Psi_d(\lambda)$. We can assume $\Psi_d(\lambda)$ is normalized. By differentiating both sides of this eigenvalue equation we obtain

$$E_d'(0) = \langle \Psi_d(0), V\Psi_d(0)\rangle \quad \text{and}$$
$$\Psi_d'(0) = -(H_0 - E_d(0))_r^{-1} P_\perp V\Psi_d(0), \quad \text{(A1)}$$

where $(H_0 - E_d(0))_r^{-1}$ is the reduced resolvent, defined on $\Psi_d(0)^\perp$, the subspace perpendicular to $\Psi_d(0)$, and $P_\perp = I - |\Psi_d(0)\rangle\langle\Psi_d(0)|$ is the projection onto $\Psi_d(0)^\perp$. By differentiating a second time and using (A1), we obtain

$$\begin{aligned} E_d''(0) &= -2\big\langle \Psi_d(0), V(H_0 - E_d(0))_r^{-1} P_\perp V\Psi_d(0)\big\rangle \\ &= -2\big\langle P_\perp V\Psi_d(0), (H_0 - E_d(0))_r^{-1} P_\perp V\Psi_d(0)\big\rangle \\ &\leq 0, \end{aligned} \quad \text{(A2)}$$

since $(H_0 - E_d(0))_r^{-1}$ is a positive operator on $\Psi_d(0)^\perp$.

This is a general argument that only requires H_0 and V to be self-adjoint and $E_d(\lambda) = \inf \sigma(H_d(\lambda)) > -\infty$ to be a simple discrete eigenvalue. So, if $\lambda \in \mathbb{R}$ and $E_d(\lambda)$ is isolated at the bottom of $\sigma(H_d(\lambda))$, then

$$E_d''(\lambda) \leq 0. \quad \text{(A3)}$$

From (A3) it follows that the graph of $E_d(\lambda)$ lies below its tangent lines. Let $L(\lambda)$ be the tangent line to $E_d(\lambda)$ at $\lambda = 0$. $L(\lambda)$ goes through the points $(0, E_d(0))$ and $(1, E_d(0) + E_d'(0))$. Note that $E_d(0) + E_d'(0)$ is the usual HF energy. Recall from (3.4) that we have $E_d(0) = 2\gamma_0 = -(Z - \frac{1}{2})^2$. So, using (3.4), we have

$$\begin{aligned} E_{HF} =: E_d(0) + E_d'(0) &= -\left(Z - \frac{1}{2}\right)^2 + \langle \Psi_d(0), V\Psi_d(0)\rangle \\ &= -\left(Z - \frac{1}{2}\right)^2 + \int\int \phi_0^2(x_1)\phi_0^2(x_2)\big(\delta(x_1 - x_2) \\ &\qquad - \phi_0^2(x_1) - \phi_0^2(x_2)\big)dx_1 dx_2 \\ &= -\left(Z - \frac{1}{2}\right)^2 - \int \phi_0^4(x)dx \\ &= -\left(Z - \frac{1}{2}\right)^2 - \left(\frac{Z}{2} - \frac{1}{6}\right) \\ &= -Z^2 + \frac{1}{2}Z - \frac{1}{12}. \end{aligned} \quad \text{(A4)}$$

From this we have

$$L(\lambda) = \left(-\frac{Z}{2} + \frac{1}{6}\right)\lambda - \left(Z - \frac{1}{2}\right)^2. \quad \text{(A5)}$$

The "Singly Ionized" Threshold

We now show that $L(\lambda) < E_{\mathrm{SI}}(\lambda)$ for $-1 \le \lambda \le 1$, provided $Z > \frac{1}{2}(1 + \frac{1}{\sqrt{3}}) \approx 0.7887$. With (3.5) and (3.7) we see that $\Psi_{\mathrm{SI}}(0) = \phi_0$ and $E_{\mathrm{SI}}(0) = -\frac{1}{2}(Z - \frac{1}{2})^2$ solve $H_{\mathrm{SI}}(\lambda)\Psi_{\mathrm{SI}}(\lambda) = E_{\mathrm{SI}}(\lambda)\Psi_{\mathrm{SI}}(\lambda)$ at $\lambda = 0$. By the argument used to prove (A3), $E''_{\mathrm{SI}}(\lambda) \le 0$. So, the graph of $E_{\mathrm{SI}}(\lambda)$ lies above its secant lines. We notice that if $Z > \frac{1}{2}\left(1 + \frac{1}{\sqrt{3}}\right) \approx 0.7887$, then

$$E_{\mathrm{HF}} = -Z^2 + \frac{1}{2}Z - \frac{1}{12} < -\frac{Z^2}{2} = E_{\mathrm{SI}}(1), \qquad \text{(A6)}$$

since $H_{\mathrm{SI}}(1)$ is a Hamiltonian with delta well potential of strength Z. Also,

$$E_d(0) = 2\gamma_0 < \gamma_0 = E_{\mathrm{SI}}(0) < 0. \qquad \text{(A7)}$$

So $E_{\mathrm{SI}}(\lambda)$ lies above the secant line through $(0, E_{\mathrm{SI}}(0))$ and $(1, E_{\mathrm{SI}}(1))$, and from (A6) and (A7), we see that this secant line lies above $L(\lambda)$ for $Z > \frac{1}{2}(1 + \frac{1}{\sqrt{3}}) \approx 0.7887$. Thus, if $Z > \frac{1}{2}(1+\frac{1}{\sqrt{3}}) \approx 0.7887$, then $E_d(\lambda) \le L(\lambda) < E_{\mathrm{SI}}(\lambda)$ for all $0 \le \lambda \le 1$. See the sketch on Figure 4.

For $-1 \le \lambda < 0$ we make the following observation:

$$\begin{aligned} H_d(\lambda) &= -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - Z[\delta(x_1) + \delta(x_2)] + \phi_0^2(x_1) \\ &\quad + \phi_0^2(x_2) + \lambda\big[\delta(x_1 - x_2) - \big(\phi_0^2(x_1) + \phi_0^2(x_2)\big)\big] \\ &= -\frac{1}{2}\frac{\partial^2}{\partial x_1^2} - Z\delta(x_1) + (1-\lambda)\phi_0^2(x_1) \\ &\quad - \frac{1}{2}\frac{\partial^2}{\partial x_2^2} - Z\delta(x_2) + (1-\lambda)\phi_0^2(x_2) \\ &\quad + \lambda\delta(x_1 - x_2) \\ &= H_{\mathrm{SI}}^{(x_1)}(\lambda) + H_{\mathrm{SI}}^{(x_2)}(\lambda) + \lambda\delta(x_1 - x_2) \\ &\le H_{\mathrm{SI}}^{(x_1)}(\lambda) + H_{\mathrm{SI}}^{(x_2)}(\lambda), \end{aligned} \qquad \text{(A8)}$$

where $H_{\mathrm{SI}}^{(x_1)}(\lambda) = -\frac{1}{2}\frac{\partial^2}{\partial x_1^2} - Z\delta(x_1) + (1-\lambda)\phi_0^2(x_1)$ is the singly ionized Hamiltonian of an electron with spatial coordinate x_1 and likewise for $H_{\mathrm{SI}}^{(x_2)}(\lambda)$. This implies that for $-1 \le \lambda < 0$, we have $E_d(\lambda) < 2E_{\mathrm{SI}}(\lambda)$ everywhere that $E_d(\lambda)$ and $E_{\mathrm{SI}}(\lambda)$ exist. So $E_d(\lambda)$ must remain a positive distance from the singly ionized threshold for $-1 \le \lambda \le 1$, if $Z > \frac{1}{2}(1 + \frac{1}{\sqrt{3}}) \approx 0.7887$.

The "Electron–Electron Bound State" Threshold

We now show that $L(\lambda) < E_{\mathrm{ee}}(\lambda) = -\frac{\lambda^2}{4}$ for $-1 \le \lambda < 0$, provided that $Z > \frac{3}{4} + \frac{\sqrt{57}}{12} \approx 1.38$. Recall that $E_d(\lambda)$ must lie on or below $L(\lambda)$. So, whenever $Z > \frac{3}{4} + \frac{\sqrt{57}}{12} \approx 1.38$ and $-1 \le \lambda < 0$,

$$\begin{aligned} E_d(\lambda) \le L(\lambda) \le L(-1) = \\ -Z^2 + \frac{3}{2}Z - \frac{5}{12} < -\frac{1}{4} \le E_{\mathrm{ee}}(\lambda), \end{aligned} \qquad \text{(A9)}$$

Thus, provided Z is above this value we know that the bound state eigenvalue stays below this threshold for $-1 \le \lambda < 0$. Refer to the sketch in Figure 5. An intersection between $E_{\mathrm{ee}}(\lambda)$ and $E_d(\lambda)$ must occur further to the left than the intersection between $E_{\mathrm{ee}}(\lambda)$ and $L(\lambda)$.

Clearly, $E_d(\lambda) \le L(\lambda) < 0$ on $-1 \le \lambda \le 1$ for Z above this value, so Theorem 3.1 is proved.

PROOF OF THEOREM 3.2

The inequality (A3) is again satisfied by $E_{\mathrm{ph}}(\lambda)$, so we have $E''_{\mathrm{ph}}(\lambda) \le 0$, and the graph of $E_{\mathrm{ph}}(\lambda)$ lies below its tangent lines. We again let $L(\lambda)$ be the tangent line at $\lambda = 0$ going through the points $(0, E_{\mathrm{ph}}(0))$ and $(1, E_{\mathrm{HF}})$. Since we do not know $\Psi_{\mathrm{ph}}(0)$, we cannot use the same argument as in the delta function model. For now we note that since $\Psi_{\mathrm{ph}}(0)$ minimizes $\langle \Psi, H_{\mathrm{ph}}(1)\Psi\rangle$ over all Slater determinants, we have

$$\begin{aligned} E_{\mathrm{HF}} = E_{\mathrm{ph}}(0) + E'_{\mathrm{ph}}(0) &= \langle \Psi_{\mathrm{ph}}(0), H_{\mathrm{ph}}(1)\Psi_{\mathrm{ph}}(0)\rangle \\ &\le \langle \phi(x_1)\phi(x_2), H_{\mathrm{ph}}(1)\phi(x_1)\phi(x_2)\rangle, \end{aligned} \qquad \text{(A10)}$$

for any normalized ϕ with $\phi(x_1)\phi(x_2)$ in the operator domain of $H_{\mathrm{ph}}(1)$.

The "Singly Ionized" Threshold

Let $E_{\mathrm{SI}}(\lambda)$ be the smallest eigenvalue of $H_{\mathrm{SI}}(\lambda)$. Again from (A3), we know that the graph of $E_{\mathrm{SI}}(\lambda)$ lies above its secant lines. Consider the trial function

$$\phi_{\mathrm{T}}(x) = \frac{1}{\sqrt{\pi}}\left(Z - \frac{5}{16}\right)^{3/2} \exp\left[-\left(Z - \frac{5}{16}\right)|x|\right].$$

Then for $Z > \frac{5}{8}(1 + \frac{1}{\sqrt{2}}) \approx 1.06694$,

$$\begin{aligned} E_{\mathrm{HF}} \leq E_{\mathrm{T}} &= \langle \phi_{\mathrm{T}}(x_1)\phi_{\mathrm{T}}(x_2), H_{\mathrm{ph}}(1)\phi_{\mathrm{T}}(x_1)\phi_{\mathrm{T}}(x_2)\rangle \\ &= -\left(Z - \frac{5}{16}\right)^2 \\ &\leq -\frac{Z^2}{2} \qquad \text{(A11)} \\ &= E_{\mathrm{SI}}(1), \qquad \text{(A12)} \end{aligned}$$

since $H_{\mathrm{SI}}(1)$ is the hydrogen atom Hamiltonian.

With (3.14) and (3.17) we obtain (A7) for this model. The graph of E_{SI} lies above the secant line through $(0, E_{\mathrm{SI}}(0))$ and $(1, E_{\mathrm{SI}}(1))$. From (A12) and (A7), we see that this line lies above $L(\lambda)$ for $Z > \frac{5}{8}(1 + \frac{1}{\sqrt{2}})$. Thus, $E_{\mathrm{ph}}(\lambda) < E_{\mathrm{SI}}(\lambda)$ on $0 \leq \lambda \leq 1$ for $Z > \frac{5}{8}(1 + \frac{1}{\sqrt{2}}) \approx 1.06694$.

For $-1 \leq \lambda < 0$ we use the same argument as in (A8). It follows that $E_{\mathrm{ph}}(\lambda)$ must remain a positive distance from $E_{\mathrm{SI}}(\lambda)$ for $-1 \leq \lambda \leq 1$, provided $Z > \frac{5}{8}(1 + \frac{1}{\sqrt{2}}) \approx 1.06694$.

The "Electron–Electron Bound State" Threshold

As in the delta function model, there is a threshold at $E_{\mathrm{ee}}(\lambda) = -\frac{\lambda^2}{4}$, if $\mathrm{Re}(\lambda) < 0$. We prove below that

$$E_{\mathrm{ph}}(0) - E'_{\mathrm{ph}}(0) < -\frac{1}{4}, \qquad \text{(A13)}$$

whenever $Z > \frac{1}{16}\left(15 + \sqrt{214}\right) \approx 1.852$. From this it follows that

$$E_{\mathrm{ph}}(\lambda) \leq L(\lambda) < -\frac{1}{4} \leq E_{\mathrm{ee}}(\lambda), \qquad \text{(A14)}$$

for $-1 \leq \lambda < 0$.

To prove (A13), we first note that (3.13) and (3.15) imply

$$\left\langle \Psi_{\mathrm{ph}}(0), \frac{1}{|x_1 - x_2|}\Psi_{\mathrm{ph}}(0)\right\rangle = \left\langle \Psi_{\mathrm{ph}}(0), \nu_i^{\mathrm{HF}}\Psi_{\mathrm{ph}}(0)\right\rangle = \left\langle \phi_0(x_i), \nu_i^{\mathrm{HF}}\phi_0(x_i)\right\rangle.$$

Then, using (3.15) and (A1), we have

$$\begin{aligned} E_{\mathrm{ph}}(0) &= 2\left\langle \phi_0, \left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\phi_0\right\rangle + 2\left\langle \phi_0(x_1), \nu_1^{\mathrm{HF}}\phi_0(x_1)\right\rangle \\ &= 2\left\langle \phi_0, \left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\phi_0\right\rangle \\ &\quad - 2\left\langle \phi_0(x_1)\phi_0(x_2), \left(\frac{1}{|x_1 - x_2|} - \nu_1^{\mathrm{HF}} - \nu_2^{\mathrm{HF}}\right) \right. \\ &\qquad \left. \times\ \phi_0(x_1)\phi_0(x_2)\right\rangle \\ &= 2\left\langle \phi_0, \left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\phi_0\right\rangle - 2E'_{\mathrm{ph}}(0) \\ &\geq 2\inf\left\{\sigma\left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\right\} - 2E'_{\mathrm{ph}}(0) \\ &= -Z^2 - 2E'_{\mathrm{ph}}(0) \qquad \text{(A15)} \end{aligned}$$

From (A12), we know that $E_{\mathrm{ph}}(0) + E'_{\mathrm{ph}}(0) \leq -\left(Z - \frac{5}{16}\right)^2$. Combining this with (A15), we obtain $E_{\mathrm{ph}}(0) - E'_{\mathrm{ph}}(0) \leq -Z^2 + \frac{15}{8}Z - \frac{75}{256}$. This implies the bound (A13). The threshold at 0 is clearly not an issue, so Theorem 3.2 is proved.

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