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Van der Waals interactions between two hydrogen atoms:
The next orders

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Abstract
We extend a method (E. Cancès and L.R. Scott, SIAM J. Math. Anal., 50, 2018, 381–410) to compute more terms in the asymptotic expansion of the van der Waals attraction between two hydrogen atoms. These terms are obtained by solving a set of modified Slater–Kirkwood partial differential equations. The accuracy of the method is demonstrated by numerical simulations and comparison with other methods from the literature. It is also shown that the scattering states of the hydrogen atom, that are the states associated with the continuous spectrum of the Hamiltonian, have a major contribution to the $C_6$ coefficient of the van der Waals expansion.

1 Introduction
Van der Waals interactions, first introduced in 1873 to reproduce experimental results on simple gases [29], have proved to also play an essential role in complex systems in the condensed phase, such as biological molecules [7, 24] and 2D materials [14]. The quantum mechanical origin of the dispersive van der Waals interaction has been elucidated by London in the 1930s [19]. The rigorous mathematical foundations of the van der Waals interaction have been investigated in the pioneering work by Lieb and Thirring [18], and later by many authors (see in particular [3, 4, 5, 6, 8, 17] and references therein).

In a recent paper [10], a new numerical approach was introduced to compute the leading order term $-C_6R^{-6}$ of the van der Waals interaction between hydrogen atoms separated by a distance $R$. Here we extend that approach to compute higher order terms $-C_nR^{-n}$, $n > 6$. The coefficients $C_n$ have been computed by various methods. On the one hand, both [22] and [12] apparently failed to include key components in the computation of $C_{10}$, computing only one component out of three that we derive here. On the other hand, our result differs by approximately 200% and agrees with [21]. One of the objects of this paper is to clarify this discrepancy.

The computation of the expansion coefficients can also be derived through techniques using polarizabilities [21] which is exact but might involve slightly different numerical computations than the perturbation method used here. In order to get the right values, one has to use a high enough order of perturbation theory. Computations using up to the second order [2, 11, 27] fail for $C_{12}$, $C_{14}$ and $C_{16}$ (with errors of approximately 1%, 5%, and 10%) for which computations up to the fourth order [20] are needed. The third order [32] is sufficient for $C_{11}$, $C_{13}$ and $C_{15}$. Moreover, the polarizabilities method can be derived also for other atoms than hydrogen as well as for three-body interaction [11]. A comparison of the numerical results is explored in Section 3.1.

One can also compute the expansion coefficients using basis states as in [13]. However, this leads to a substantial error even for $C_6$. The discrepancy observed between the basis states method and the other methods can be interpreted as the missing contribution to the energy from the continuous spectrum.

The perturbation method of [26] is remarkable because, in the case of two hydrogen atoms, the problem splits, for any of the $C_n$ terms, exactly into terms constituted of an angular factor and a function of two one-dimensional variables (the underlying problem is six-dimensional). The
first term in this expansion has been examined in [10] and gave a value of $C_6$ agreeing with [21]. This article extends this analysis and allows computation of all $C_n$. The linearity and the nature of the angular parts allows treatment of these problems separately in a way analogous to the first term of the expansion. Although the partial differential equations (PDE) defining the functions of these two variables are not solvable in closed form, they are nevertheless easily solved by numerical techniques.

In Section 2, we present an extended and modified version of Slater and Kirkwood’s derivation, in order to manipulate more suitable family of PDEs for theoretical analysis and numerical simulation. These modified Slater–Kirkwood PDEs are well posed at all orders and, when their unique solutions are multiplied by their respective angular factor, the resulting function, after summation of the terms, solves the triangular systems of six-dimensional PDEs originating from the Rayleigh–Schrödinger expansion. We finally check that the so-obtained perturbation series are asymptotic expansions of the ground state energy and wave function (after applying some “almost unitary” transform) of the hydrogen molecule in the dissociation limit. In Section 3, we use a Laguerre approximation [25, Section 7.3] to compute coefficients up to $C_{19}$, given that $C_6$ has been computed in [10]. Our approach also allows us to evaluate the respective contributions of the bound and scattering states of the Hamiltonian of the hydrogen atom to the $C_6$ coefficient of the van der Waals interaction. Numerical simulations show that the terms in the sum-over-states expansion coupling two bound states only contribute to about 60%. The mathematical proofs are gathered in Section 4. Lastly, some useful results on the multipolar expansion of the hydrogen molecule electrostatic potential in the dissociation limit and on the Wigner $(2n + 1)$ rule used in the computations are provided in the Appendix.

2 The hydrogen molecule in the dissociation limit

As usual in atomic and molecular physics, we work in atomic units: $\hbar = 1$ (reduced Planck constant), $\epsilon = 1$ (elementary charge), $m_e = 1$ (mass of the electron), $\epsilon_0 = 1/(4\pi)$ (dielectric permittivity of the vacuum). The length unit is the bohr (about 0.529 Ångstroms) and the energy unit is the hartree (about $4.36 \times 10^{-18}$ Joules).

We study the Born-Oppenheimer approximation of a system of two hydrogen atoms, consisting of two classical point-like nuclei of charge 1 and two quantum electrons of mass 1 and charge $-1$. Let $r_1$ and $r_2$ be the positions in $\mathbb{R}^3$ of the two electrons, in a cartesian frame whose origin is the center of mass of the nuclei. We denote by $e$ the unit vector pointing in the direction from one hydrogen atom to the other, and by $R$ the distance between the two nuclei. We introduce the parameter $\epsilon = R^{-1}$ and derive expansions in $\epsilon$ of the ground state energy and wave function. Note that in [10], we use instead $\epsilon = R^{-1/3}$. The latter is well-suited to compute the lower-order coefficient $C_6$, but the change of variable $\epsilon = R^{-1}$ is more convenient to compute all the terms of the expansion.

Since the ground state of the hydrogen molecule is a singlet spin state [15], its wave function can be written as

$$\psi_\epsilon(r_1, r_2) = \frac{|\uparrow\downarrow| - |\downarrow\uparrow|}{\sqrt{2}},$$

where $\psi_\epsilon > 0$ is the $L^2$-normalized ground state of the spin-less six-dimensional Schrödinger equation

$$H_\epsilon \psi_\epsilon = \lambda_\epsilon \psi_\epsilon, \quad \|\psi_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1,$$

where for $\epsilon > 0$, the Hamiltonian $H_\epsilon$ is the self-adjoint operator on $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3 \times \mathbb{R}^3)$ defined by

$$H_\epsilon = -\frac{1}{2} \Delta_{r_1} - \frac{1}{2} \Delta_{r_2} - \frac{1}{|r_1 - (2\epsilon)^{-1} e|} - \frac{1}{|r_2 - (2\epsilon)^{-1} e|} - \frac{1}{|r_1 + (2\epsilon)^{-1} e|} - \frac{1}{|r_2 + (2\epsilon)^{-1} e|} + \frac{1}{|r_1 - r_2|},$$

where $\Delta_{r_k}$ is the Laplace operator with respect to the variables $r_k \in \mathbb{R}^3$. The first two terms of $H_\epsilon$ model the kinetic energy of the electrons, the next four terms the electrostatic attraction between nuclei and electrons, and the last two terms the electrostatic repulsion between, respectively, electrons and nuclei. The ground state of $H_\epsilon$ is symmetric ($\psi_\epsilon(r_1, r_2) = \psi_\epsilon(r_2, r_1)$) so that the wave
function defined by (1) does satisfy the Pauli principle (the anti-symmetry is entirely carried by the spin component). It is well-known [10] that

\[ \lambda_\epsilon = -1 - C_\epsilon e^6 + o(e^6). \]

The computation of \( \lambda_\epsilon \) (and \( \psi_\epsilon \)) to higher order by a modified version of the Slater–Kirkwood approach, is the subject of this article.

2.1 Perturbation expansion

The first step is to make a change of coordinates. Introducing the translation operator

\[ \tau \epsilon f(r_1, r_2) = f(r_1 + (2\epsilon)^{-1} e, r_2 - (2\epsilon)^{-1} e) = f(r_1 + \frac{1}{2}\epsilon e, r_2 - \frac{1}{2}\epsilon e), \quad R = \epsilon^{-1}, \]

the swapping operator \( \mathcal{C} \) and the symmetrization operator \( S \) defined by

\[ \mathcal{C} \phi(r_1, r_2) = \phi(r_2, r_1), \quad S = \frac{1}{\sqrt{2}}(\mathcal{I} + \mathcal{C}), \]

where \( \mathcal{I} \) denotes the identity operator, as well as the “asymptotically unitary” operator

\[ \mathcal{T}_\epsilon = S \tau \epsilon. \tag{3} \]

It is shown in [10] that

\[ H_\epsilon \mathcal{T}_\epsilon = \mathcal{T}_\epsilon H_0 + V_\epsilon, \tag{4} \]

where \( H_0 \) is the reference non-interacting Hamiltonian

\[ H_0 = -\frac{1}{2} \Delta r_1 - \frac{1}{|r_1|} - \frac{1}{2} \Delta r_2 - \frac{1}{|r_2|}, \]

and \( V_\epsilon \) the correlation potential

\[ V_\epsilon(r_1, r_2) = -\frac{1}{|r_1 - \epsilon e|} - \frac{1}{|r_2 + \epsilon e|} + \frac{1}{|r_1 - r_2 - \epsilon^2 e|} + \epsilon. \tag{5} \]

The linear operator \( \mathcal{T}_\epsilon \) is “asymptotically unitary” in the sense that for all \( f, g \in L^2(\mathbb{R}^3 \times \mathbb{R}^3) \),

\[ \langle \mathcal{T}_\epsilon f, \mathcal{T}_\epsilon g \rangle = \langle f, g \rangle + \langle C f, \tau_\epsilon g \rangle \xrightarrow{\epsilon \to 0} \langle f, g \rangle. \]

It follows from (4) that if \( (\lambda, \phi) \) is a normalized eigenstate of \( H_0 + V_\epsilon \), that is \( (\lambda, \phi) \) satisfies

\[ (H_0 + V_\epsilon)\phi = \lambda \phi, \quad \|\phi\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1, \]

then

\[ H_\epsilon \mathcal{T}_\epsilon \phi = \lambda \mathcal{T}_\epsilon \phi. \]

In addition, we know from Zhislin’s theorem [10, 33] that both \( H_\epsilon \) and \( H_0 + V_\epsilon \) have ground states, that their ground state eigenvalues are non-degenerate, and that their ground state wave functions are (up to replacing them by their opposites) positive everywhere in \( \mathbb{R}^3 \times \mathbb{R}^3 \). Since \( \mathcal{T}_\epsilon \) preserves positivity, we infer that \( H_\epsilon \) and \( H_0 + V_\epsilon \) share the same ground state eigenvalue \( \lambda_\epsilon \) and that if \( \phi_\epsilon \) is the normalized positive ground state wave function of \( H_0 + V_\epsilon \), then \( \psi_\epsilon := \mathcal{T}_\epsilon \phi_\epsilon / \|\mathcal{T}_\epsilon \phi_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \) is the normalized positive ground state wave function of \( H_\epsilon \).

The next step is to construct for \( \epsilon > 0 \) small enough the ground state \( (\lambda_\epsilon, \phi_\epsilon) \) of \( H_0 + V_\epsilon \) by the Rayleigh–Schrödinger perturbation method from the explicit ground state

\[ \lambda_0 = -1, \quad \phi_0(r_1, r_2) = \pi^{-1} e^{-\left(|r_1| + |r_2|\right)}, \tag{6} \]

of \( H_0 \). Using a multipolar expansion, we have

\[ V_\epsilon(r_1, r_2) = \sum_{n=3}^{+\infty} c^n B^{(n)}(r_1, r_2), \tag{7} \]
where homogeneous polynomial functions $B^{(n)}$, $n \geq 3$ are specified below (see equation (14)), the convergence of the series being uniform on every compact subset of $\mathbb{R}^3 \times \mathbb{R}^3$. Assuming that $\lambda_\varepsilon$ and $\phi_\varepsilon$ can be Taylor expanded as

$$\lambda_\varepsilon = \lambda_0 - \sum_{n=1}^{+\infty} C_n \varepsilon^n \quad \text{and} \quad \phi_\varepsilon = \sum_{n=0}^{+\infty} \varepsilon^n \phi_n, \quad \text{(formal expansions)} \quad (8)$$

(we use the standard historical notation $-C_n$ instead of $\lambda_n$ for the coefficients of the eigenvalue $\lambda_\varepsilon$) inserting these expansions in the equations $(H_0 + V_\varepsilon)\phi_\varepsilon = \lambda_\varepsilon \phi_\varepsilon$, $\|\phi_\varepsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1$, and identifying the terms of order $n$ in $\varepsilon$, we obtain a triangular system of linear elliptic equations (Rayleigh–Schrödinger equations). The well-posedness of this system is given by the following lemma, whose proof is postponed until Section 4.2.

Lemma 1. The triangular system

$$\forall n \geq 1, \quad (H_0 - \lambda_0)\phi_n = -\sum_{k=3}^{n} B^{(k)}(\phi_{n-k}) - \sum_{k=1}^{n} C_k \phi_{n-k}, \quad (9)$$

$$\langle \phi_0, \phi_n \rangle = -\frac{1}{2} \sum_{k=1}^{n-1} \langle \phi_k, \phi_{n-k} \rangle, \quad (10)$$

where we use the convention $\sum_{k=m}^{n} \cdots = 0$ if $m > n$, has a unique solution $((C_n, \phi_n))_{n \in \mathbb{N}}$ in $(\mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3))^N$. In particular, we have $(C_1, \phi_1) = (C_2, \phi_2) = 0$ and $C_3 = C_4 = C_5 = 0$. In addition, the functions $\phi_n$ are real-valued.

Note that $(C_1, \phi_1) = (C_2, \phi_2) = 0$ directly follows from the fact that the first non-vanishing term in the expansion (7) of $V_\varepsilon$ is $\varepsilon^3 B^{(3)}$. The formal expansions (8) are in fact asymptotic expansions as established in the following theorem. Its proof is provided in Section 4.2.

Theorem 2. Let $\psi_\varepsilon \in H^2(\mathbb{R}^3 \times \mathbb{R}^3)$ be the positive $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$-normalized ground state of $H_\varepsilon$ and $\lambda_\varepsilon$ the associated ground-state energy:

$$H_\varepsilon \psi_\varepsilon = \lambda_\varepsilon \psi_\varepsilon, \quad \|\psi_\varepsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1, \quad \psi_\varepsilon > 0 \text{ a.e. on } \mathbb{R}^3 \times \mathbb{R}^3. \quad (11)$$

Let $(\phi_0, \lambda_0)$ be as in (6), $((C_n, \phi_n))_{n \in \mathbb{N}}$, the unique solution of (9) in $(\mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3))^N$, and $T_\varepsilon$ the “almost unitary” symmetrization operator defined in (3). Then, for all $n \in \mathbb{N}$, there exists $\varepsilon_n > 0$ and $K_n \in \mathbb{R}_+$ such that for all $0 < \varepsilon \leq \varepsilon_n$,

$$\left\| \psi_\varepsilon - \psi_\varepsilon^{(n)} \right\|_{H^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq K_n \varepsilon^{n+1}, \quad \left| \lambda_\varepsilon - \lambda_\varepsilon^{(n)} \right| \leq K_n \varepsilon^{n+1}, \quad \left| \lambda_\varepsilon - \lambda_\varepsilon^{(n)} \right| \leq K_n \varepsilon^{2(n+1)}, \quad (12)$$

where

$$\psi_\varepsilon^{(n)} := \frac{T_\varepsilon (\phi_0 + \sum_{k=3}^{n} \varepsilon^k \phi_k)}{\|T_\varepsilon (\phi_0 + \sum_{k=3}^{n} \varepsilon^k \phi_k)\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}}, \quad \lambda_\varepsilon^{(n)} := \lambda_0 - \sum_{k=3}^{n} C_k \varepsilon^k, \quad \mu_\varepsilon^{(n)} = \langle \psi_\varepsilon^{(n)} | H_\varepsilon | \psi_\varepsilon^{(n)} \rangle.$$

Let us point out that in view of the last two bounds in (12), the series expansion of $\mu_\varepsilon^{(n)}$ in $\varepsilon$ up to order $(2n + 1)$, which can be computed from the $\phi_k$’s for $0 \leq k \leq n$, is given by

$$\mu_\varepsilon^{(n)} = \lambda_0 - \sum_{k=6}^{2n+1} C_k \varepsilon^k + O(\varepsilon^{2n+2}).$$

Therefore, the knowledge of the $\phi_k$’s up to order $n$ allows one to compute all the $C_k$’s up to order $(2n + 1)$ (Wigner’s $(2n + 1)$ rule).

Remark 3 (van der Waals forces). It follows from the Hellmann–Feynman theorem that the van der Waals force $F_\varepsilon$ acting on the nucleus located at $(2\varepsilon)^{-1}e$ is given by

$$F_\varepsilon = \int_{\mathbb{R}^3} \frac{r - (2\varepsilon)^{-1}e}{|r - (2\varepsilon)^{-1}e|^3} \rho_\varepsilon(r) \, dr \quad \text{with} \quad \rho_\varepsilon(r) = 2 \int_{\mathbb{R}^3} |\psi_\varepsilon(r, r')|^2 \, dr' \quad \text{(electronic density).}$$
Introducing the approximation \( F^{(n)}_e \) of \( F_e \) computed from \( \psi^{(n)}_e \) as

\[
F^{(n)}_e = \int_{\mathbb{R}^3} \frac{(r - (2 \epsilon)^{-1} e)}{|r - (2 \epsilon)^{-1} e|^3} \rho^{(n)}_e(r) \, dr \quad \text{with} \quad \rho^{(n)}_e(r) = 2 \int_{\mathbb{R}^3} |\psi^{(n)}_e(r, r')|^2 \, dr',
\]

we obtain from the Cauchy-Schwarz inequality, the Hardy inequality in \( \mathbb{R}^3 \), and (12) that

\[
|F_e - F^{(n)}_e| \leq 8 \| \psi_e - \psi^{(n)}_e \|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \| \psi_e + \psi^{(n)}_e \|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq K_n \epsilon^{n+1}
\]

for some constant \( K_n \in \mathbb{R}_+ \) independent of \( \epsilon \) and \( \epsilon \) small enough. Since \( F^{(n)}_e \) can be Taylor expanded at \( \epsilon = 0 \), we obtain that the force \( F_e \) satisfies for all \( n \geq 6 \)

\[
F_e = - \left( \sum_{k=6}^{n} nC_n \epsilon^{n+1} \right) e + O(\epsilon^{n+1}).
\]

This extends the result \( F_e = -6C_6 \epsilon^7 e + O(\epsilon^8) \) proved in [5, Theorem 4] for any two atoms with non-degenerate ground states, to arbitrary order in the simple case of two hydrogen atoms.

### 2.2 Computation of the perturbation series

The coefficients \( B^{(n)} \) are obtained by a classical multipolar expansion, detailed in Appendix A.1 for the sake of completeness. Using spherical coordinates in an orthonormal cartesian basis \( (e_1, e_2, e_3) \) of \( \mathbb{R}^3 \) for which \( e_3 = e \), so that

\[
r_i = r_i \sin(\theta_i) \cos(\phi_i) e_1 + \sin(\theta_i) \sin(\phi_i) e_2 + \cos(\theta_i) e_3,
\]

\[
\cos(\theta_i) = r_i \cdot e, \quad \text{and} \quad r_i = |r_i|, \quad i = 1, 2,
\]

it holds that for all \( n \geq 3 \),

\[
B^{(n)}(r_1, r_2) = \sum_{(l_1, l_2) \in B_n} \sum_{l_1, l_2 \geq 0} \sum_{m \leq |l_1 - l_2|} G_c(l_1, l_2, m) Y^m_{l_1}(\theta_1, \phi_1) Y^{m*}_{l_2}(\theta_2, \phi_2),
\]

\[
= \sum_{(l_1, l_2) \in B_n} \sum_{l_1, l_2 \geq 0} \sum_{m \leq |l_1 - l_2|} G_r(l_1, l_2, m) Y^m_{l_1}(\theta_1, \phi_1) Y^{m*}_{l_2}(\theta_2, \phi_2),
\]

where \( (Y^m_l)_{l \in \mathbb{N}, m = -l, \ldots, l} \) and \( (\bar{Y}^m_l)_{l \in \mathbb{N}, m = -l, \ldots, l} \) are respectively the complex and real spherical harmonics, and where

\[
B_n = \{(l_1, l_2) : l_1 + l_2 = n - 1, l_1, l_2 \neq 0\} = \{(l, n - 1 - l) : 1 \leq l \leq n - 2\}.
\]

The coefficients \( G_c(l_1, l_2, m) \) and \( G_r(l_1, l_2, m) \) are respectively given by

\[
G_c(l_1, l_2, m) := (-1)^{l_2} \frac{4\pi(l_1 + l_2)!}{(2l_1 + 1)(2l_2 + 1)(l_1 - m)!(l_1 + m)!(l_2 - m)!(l_2 + m)!}^{1/2},
\]

\[
G_r(l_1, l_2, m) := (-1)^m G_c(l_1, l_2, m).
\]

Both expansions (14) and (15) are useful: (14) will be used in the proof of Theorem 5 to establish formula (26), which has a simpler and more compact form in the complex spherical harmonics basis. On the other hand, (15) allows one to work with real-valued functions.

One of the main contributions of this article is to show that the functions \( \phi_n \), hence the real numbers \( \lambda_n \), can be obtained by solving simple 2D linear elliptic boundary value problems on the quadrant

\[
\Omega = \mathbb{R}_+^+ \times \mathbb{R}_+^+.
\]

For each angular momentum quantum number \( l \in \mathbb{N} \), we denote by

\[
\kappa_l(r) = \frac{(l + 1)}{2r^2} - \frac{1}{r} - \frac{1}{2} \lambda_0 = \frac{l(l + 1)}{2r^2} - \frac{1}{r} + \frac{1}{2},
\]

(18)
and we consider the boundary value problem: given \( f \in L^2(\Omega) \)
\[
\begin{align*}
\begin{cases}
\text{find } T \in H_0^1(\Omega) \text{ such that } \\
-\frac{1}{2} \Delta T(r_1, r_2) + (\kappa_1(r_1) + \kappa_2(r_2)) T = f(r_1, r_2) \quad \text{in } \mathcal{D}'(\Omega).
\end{cases}
\end{align*}
\]  
(19)

It follows from classical results on the radial operator \(-\frac{1}{2} \frac{d^2}{dr^2} + \kappa_l\) on \( L^2(0, +\infty) \) with form domain \( H_0^1(0, +\infty) \) encountered in the study of the hydrogen atom (see Section 4.1 for details) that for all \( l_1, l_2 \in \mathbb{N}, (l_1, l_2) \neq (0, 0) \), the problem (19) is well posed in \( H_0^1(\Omega) \). For \( l_1 = l_2 = 0 \), this problem is well-posed in
\[
\tilde{H}_0^1(\Omega) = \left\{ v \in H_0^1(\Omega) : \int_{\Omega} v(r_1, r_2) e^{-r_1-r_2} r_1 r_2 dr_1 dr_2 = 0 \right\},
\]
provided that the compatibility condition
\[
\int_{\Omega} f(r_1, r_2) e^{-r_1-r_2} r_1 r_2 dr_1 dr_2 = 0
\]  
(20)
is fulfilled. Problem (19) is useful to solve the Rayleigh–Schrödinger system (9)-(10) thanks to the following lemma, proved in Section 4.1. We denote by
\[
\phi_0^+ := \left\{ \psi \in L^2(\mathbb{R}^3 \times \mathbb{R}^3) : \langle \phi_0, \psi \rangle = 0 \right\}.
\]
Note that the condition (20) is equivalent to \( \langle \phi_0, \frac{f(r_1, r_2)}{r_1 r_2} \rangle = 0 \).

**Lemma 4.** Let \( l_1, l_2 \in \mathbb{N}, m_1, m_2 \in \mathbb{Z} \) such that \(-l_j \leq m_j \leq l_j\) for \( j = 1, 2 \), and \( f \in L^2(\Omega) \). Consider the problem of finding \( \psi \in H^2(\mathbb{R}^3 \times \mathbb{R}^3) \cap \phi_0^+ \) solution to the equation
\[
(H_0 - \lambda_0) \psi = F \quad \text{with} \quad F := \frac{f(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2).
\]  
(21)

1. If \((l_1, l_2) \neq (0, 0)\), then the unique solution to (21) in \( H^2(\mathbb{R}^3 \times \mathbb{R}^3) \) is
\[
\psi = \frac{T(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2),
\]  
(22)
where \( T \) is the unique solution to (19) in \( H_0^1(\Omega) \);

2. If \((l_1, l_2) = (0, 0)\), and if the compatibility condition (20) is satisfied, then the unique solution to (21) in \( H^2(\mathbb{R}^3 \times \mathbb{R}^3) \cap \phi_0^+ \) is
\[
\psi = \frac{1}{4\pi} \frac{T(r_1, r_2)}{r_1 r_2},
\]
where \( T \) is the unique solution to (19) in \( \tilde{H}_0^1(\Omega) \).

In addition, if \( f \) decays exponentially at infinity, then so does \( T \), hence \( \psi \), in the following sense: for all \( 0 \leq \alpha < \sqrt{3}/8 \), there exists a constant \( C_\alpha \in \mathbb{R}_+ \) such that for all \( \eta > \alpha, l_1, l_2 \in \mathbb{N} \), \( m_1, m_2 \in \mathbb{Z} \) such that \(-l_j \leq m_j \leq l_j\) for \( j = 1, 2 \), and all \( f \in L^2(\Omega) \)
\[
\|e^{\alpha(r_1+r_2)} T\|_{H^1(\Omega)} \leq C_\alpha \|e^{\eta(r_1+r_2)} f\|_{L^2(\Omega)},
\]  
(23)
\[
\|e^{\alpha(|r_1|+|r_2|)} \psi\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C_\alpha \|e^{\eta(|r_1|+|r_2|)} F\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)},
\]  
(24)
\[
\|e^{\alpha(|r_1|+|r_2|)} \psi\|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C_\alpha (1 + 4L_1(l_1+1) + 4L_2(l_2+1))^{1/2} \|e^{\eta(|r_1|+|r_2|)} F\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}.
\]  
(25)
Lastly, if \( f \) is real-valued, then so is \( T \).

The properties of the functions \( \phi_0 \), upon which our numerical method is based, are collected in the following theorem, proved in Section 4.2.
Theorem 5. Let \((C_n, φ_n)_{n \in \mathbb{N}^*}\) be the unique solution in \((\mathbb{R} \times H^2(\mathbb{R}^2 \times \mathbb{R}^2))_{n \in \mathbb{N}^*}\) to the Rayleigh–Schrödinger system (9). Then, \(φ_1 = φ_2 = 0, C_n = 0\) for \(1 \leq n \leq 5\) and for each \(n \geq 3\), there exists a positive integer \(N_n\) such that

\[
φ_n = \sum_{(l_1, l_2) \in \mathcal{L}_n} \frac{T^{(n)}_{(l_1, l_2)}(r_1, r_2)}{r_1 r_2} \left( \sum_{m = -\min(l_1, l_2)}^{\min(l_1, l_2)} \alpha^{(n)}_{(l_1, l_2, m)} Y^{m}_l(θ_1, φ_1)Y^{−m}_l(θ_2, φ_2) \right),
\]

where \(\mathcal{L}_n\) is a finite subset of \(\mathbb{N}^2\) with cardinality \(N_n < \infty\), where \(T^{(n)}_{(l_1, l_2)}\) is the unique solution to (19) in \(H^1(Ω)\) (or in \(\bar{H}^1(Ω)\) if \(l_1 = l_2 = 0\)) for \(f = f^{(n)}_{(l_1, l_2)}\), where \(f^{(n)}_{(l_1, l_2)}\) is a real-valued function that can be computed recursively from the \(T^{(n)}_{(l_1, l_2)}\)'s, for \(n < n'\), and where \(\alpha^{(n)}_{(l_1, l_2, m)}\) are real coefficients. Moreover, there exists \(α_n > 0\) such that

\[
\left\| e^{α_n(r_1 + r_2)} T^{(n)}_{(l_1, l_2)} \right\|_{H^1(Ω)} < \infty,
\]

\[
\left\| e^{α_n(|r_1| + |r_2|)} φ_n \right\|_{H^1(\mathbb{R}^3 × \mathbb{R}^3)} < \infty.
\]

The number \(N_n = |\mathcal{L}_n|\) (number of terms in the expansion) for \(6 \leq n \leq 9\) are displayed in Table 1, whose construction rules are given in the proof of Theorem 5 (see Section 4.2). For \(3 \leq n \leq 5\), \(\mathcal{L}_n = B_n\), where the latter set is defined in (16), and \(N_n = |B_n| = n − 2\). For general \(n, B_n \subset \mathcal{L}_n\). For \(n \geq 6\), additional terms appear, as indicated in Table 1.

| \(n\) | \(N_n\) | pairs of angular momentum quantum numbers \((l_1, l_2)\) in \(\mathcal{L}_n \setminus B_n\) |
|-----|-----|-----------------------------|
| 6   | 8   | \((0,2;0,2)\)               |
| 7   | 13  | \((0,2;1,3), (1,3;0,2)\)    |
| 8   | 18  | \((0,2;0,2), (1,3;1,3), (0,2;4;0,2)\) |
| 9   | 27  | \((0,2;1,3,5), (1,3;0,2,4), (1,3;5;0,2), (0,2;4;1,3), (1,3;1,3)\) |

Table 1: Additional spherical harmonics appearing in each \(φ_n\) for \(6 \leq n \leq 9\). \(N_n\) is the number of terms in the spherical harmonics expansion (26). The condensed notation \((l_1, l'_1; l_2, l'_2)\) (resp. \((l_1, l'_1; l'_2, l'_2)\) or \((l_1, l'_1; l''_2, l'_2)\)) stands for the four (resp. six) pairs \((l_1, l_2), (l'_1, l_2), (l_1, l'_2),\) etc.

Table 1 can be read using the following rule: for a given \(n\), if \((l_1, l_2)\) appears in the corresponding row of the table, then there may exist \(m\) such that \(Y^m_l(θ_1, φ_1)Y^{-m}_l(θ_2, φ_2)\) might appear with a non-zero coefficient \(α^{(n)}_{(l_1, l_2, m)}\) in the spherical harmonics expansion (26) of \(φ_n\). Conversely, if a given \((l_1, l_2)\) does not appear in the table, then \(\langle φ_n, \frac{n!(r_1 + r_2)}{r_1 r_2} Y^m_l(θ_1, φ_1)Y^{-m}_l(θ_2, φ_2) \rangle = 0\), for all \(m_1, m_2\) and all \(v \in L^2(Ω)\). The relative complexity of Table 1 is due to the fact that the first term in the right-hand side of (9) is a sum of bilinear terms in \(B^{(k)}\) and \(φ_{n−k}\). The angular parts of both \(B^{(k)}\) and \(φ_{n−k}\) are finite linear combinations of angular basis functions \(Y^m_l \otimes Y^{-m}_l\). When multiplied, they give rise to a still finite but longer linear combination of \(Y^m_l \otimes Y^{-m}_l\)’s (see (69)). By contrast, the corresponding table for the \(B^{(n)}\)’s is quite simple, since all the rows have the same structure: for all \(n \geq 3\), we have

\[
n \quad n−2 \quad (k, n−k) \quad \text{for} \quad 1 \leq k \leq n−2.
\]

From \((φ_k)_{0 \leq k \leq n}\), we can obtain the coefficients \(λ_j\) up to \(j = 2n + 1\) using Wigner’s \((2n + 1)\) rule. Another, more direct, way to compute recursively the \(λ_n\)’s is to take the inner product of \(φ_n\) with each side of (9) and use the fact that \(\langle φ_n, (H_0 − λ_n)φ_n \rangle = \langle (H_0 − λ_n)φ_n, φ_n \rangle = 0\). Since \((C_1, φ_1) = (C_2, φ_2) = 0\), we thus obtain

\[
C_n = −\sum_{k=3}^{n−3} \langle φ_0, B^{(k)}φ_{n−k} \rangle - \sum_{k=3}^{n−3} C_k \langle φ_0, φ_{n−k} \rangle,
\]

where we use the convention \(\sum_{k=m}^{n} \cdots = 0\) if \(m > n\). It follows that \(C_3 = C_4 = C_5 = 0\).
Using (14), (26) and the orthonormality properties of the complex spherical harmonics, the terms \( \langle \phi_0, B^{(k)} \phi_{n-k} \rangle \) in (30) can be written as

\[
\langle \phi_0, B^{(k)} \phi_{n-k} \rangle = \langle B^{(k)} \phi_0, \phi_{n-k} \rangle = \sum_{l_1,l_2 \in B_k} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} G_c(l_1,l_2,m) Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2) \pi^{-1} e^{-(r_1+r_2)},
\]

\[
= - \sum_{(l_1,l_2) \in L_{n-k} \cap B_k} \beta_{l_1,l_2}^{(n-k)} \langle \phi_{n-k}, \phi_{l_1,l_2} \rangle,
\]

where

\[
\beta_{l_1,l_2}^{(n)} := -\pi^{-1} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \alpha_{l_1,l_2,m}^{(n)} G_c(l_1,l_2,m)
\]

\[
\ell_{l_1,l_2}^{(n)} := \int_{r_1}^l r_1^1 + r_2^{l_2+1} e^{-(r_1+r_2)} T_{l_1,l_2}^{(n)}(r_1,r_2) dr_1 dr_2,
\]

with the convention that \( \beta_{l_1,l_2}^{(n)} \langle \phi_{n-k}, \phi_{l_1,l_2} \rangle = 0 \) if \( (l_1, l_2) \notin L_n \). In view of Table 1, we see in particular that since the sum in (31) is empty

\[
\langle \phi_0, B^{(k)} \phi_n \rangle = 0 \quad \forall \, k, n = 3, 4, 5, k \neq n,
\]

and that many other vanish, e.g.

\[
\langle \phi_0, B^{(3)} \phi_0 \rangle = 0, \quad \langle \phi_0, B^{(4)} \phi_5 \rangle = 0, \quad \langle \phi_0, B^{(5)} \phi_4 \rangle = 0, \quad \langle \phi_0, B^{(6)} \phi_3 \rangle = 0.
\]

Additional pairs \( k, n \) can be examined by comparing the sets \( B_k \) and \( L_{n-k} \).

Furthermore, if the chosen numerical method to solve the boundary value problem (19) giving the radial function \( T_{l_1,l_2}^{(n-k)} \) is a Galerkin method using as basis functions of the approximation space tensor products of 1D Laguerre functions (that are, polynomials in \( r \) times \( e^{-r} \)), then the computation of \( \ell_{l_1,l_2}^{(n)} \) can be done explicitly, at least for the approximate solution [25, Section 7.3]. Using the fact that

\[
\phi_0 = 4 e^{-(r_1+r_2)} Y_0^0(\theta_1, \phi_1) Y_0^0(\theta_2, \phi_2),
\]

we then have

\[
\langle \phi_0, \phi_n \rangle = \left\langle 4 e^{-(r_1+r_2)} Y_0^0(\theta_1, \phi_1) Y_0^0(\theta_2, \phi_2), \sum_{(l_1,l_2) \in L_n} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} T_{l_1,l_2}^{(n)}(r_1,r_2) \right\rangle \pi^{-1} e^{-(r_1+r_2)}
\]

\[
= 4 \alpha_{(0,0,0)}^{(0)} \beta_{(0,0)}^{(n)}
\]

As a consequence, \( \langle \phi_0, \phi_n \rangle = 0 \) if \( (0, 0) \notin L_n \), so that in particular

\[
\langle \phi_0, \phi_3 \rangle = \langle \phi_0, \phi_4 \rangle = \langle \phi_0, \phi_5 \rangle = 0.
\]

Then, \( C_n \) can be computed from (30) as

\[
C_n = \sum_{k=3}^{n-3} \sum_{(l_1,l_2) \in L_{n-k}} \beta_{l_1,l_2}^{(n-k)} \ell_{l_1,l_2}^{(n-k)} - 4 \sum_{k=6}^{n-3} C_k \alpha_{(0,0,0)}^{(n-k)} \beta_{(0,0)}^{(n-k)}
\]

\[
+ \sum_{l_1,l_2 \neq 0} \beta_{l_1,l_2}^{(n-k)} \ell_{l_1,l_2}^{(n-k)}
\]
2.3 Practical computation of the lowest order terms

We detail in this section the practical computation of $\phi_3$ (already done in [10]), $\phi_4$ and $\phi_5$, as well as $C_n$ for $n \leq 11$. Recall that $\phi_1 = \phi_2 = 0$, and $C_n = 0$ for $n \leq 5$.

Computation of $\phi_3$. We have

$$B^{(3)} = r_1r_2 \left( \sum_{m=-1}^{1} G_c(1, m) Y_1 \theta \phi_1 Y_1^{-m} \theta_2 \phi_2 \right), \quad (40)$$

$$(H_0 - \lambda_0)\phi_3 = -B^{(3)}\phi_0, \quad (41)$$

$$\langle \phi_0, \phi_3 \rangle = 0, \quad (42)$$

with $G_c(1, m) = -\frac{1}{4}(8 - 4|m|)$ and therefore

$$(H_0 - \lambda_0)\phi_3 = -r_1r_2 e^{-(r_1 + r_2)} \left( \sum_{m=-1}^{1} \pi^{-1} G_c(1, m) Y_1 \theta \phi_1 Y_1^{-m} \theta_2 \phi_2 \right),$$

$$\langle \phi_0, \phi_3 \rangle = 0.$$

As a consequence, using Lemma 4, it holds that $L_3 = \{(1,1)\}$,

$$\phi_3 = T^{(3)} \left( \frac{r_1 r_2}{r_1 r_2} \sum_{m=-1}^{1} \alpha^{(3)} \left( c_{1,1,m} \right) Y_1 \theta \phi_1 Y_1^{-m} \theta_2 \phi_2 \right), \quad (43)$$

where $\alpha^{(3)}(c_{1,1,m}) = -\pi^{-1} G_c(1, 1, m) = -\frac{1}{4}(8 - 4|m|)$ and where $T^{(3)}(1,1,1) \in L_0^1(\Omega)$ can be numerically computed by solving the 2D boundary value problem

$$-\frac{1}{2} \Delta T^{(3)}(1,1,1) + (\kappa_1(r_1) + \kappa_1(r_2)) T^{(3)}(1,1,1) = r_1^2 r_2 e^{-(r_1 + r_2)} \quad \text{in } \Omega$$

with homogeneous Dirichlet boundary conditions.

Computation of $\phi_4$. To compute the next order, we first expand $B^{(4)}$ as

$$B^{(4)} = r_1 r_2 \sum_{m=-1}^{1} G_c(1, 2, m) Y_1 \theta \phi_1 Y_2^{-m} \theta_2 \phi_2 + r_2^2 \sum_{m=-2}^{2} G_c(2, 1, m) Y_1 \theta \phi_1 Y_2^{-m} \theta_2 \phi_2,$$

with $G_c(1, 2, 1) = G_c(1, 2, -1) = 4\pi/\sqrt{5}$, $G_c(1, 2, 0) = 4\pi\sqrt{3}/\sqrt{5}$, $G_c(2, 1, m) = -G_c(1, 2, m)$. From (9)-(10), we get

$$(H_0 - \lambda_0)\phi_4 = -B^{(3)}\phi_1 - B^{(4)}\phi_0,$$

$$\langle \phi_0, \phi_4 \rangle = 0,$$

since $\phi_1 = \phi_2 = 0$ and $C_k = 0$ for $1 \leq k \leq 5$. We therefore have $L_4 = \{(1,2), (2,1)\}$ and

$$\phi_4 = \frac{T^{(4)}(r_1, r_2)}{e_{r_1 r_2}} \sum_{m=-1}^{1} \alpha^{(4)} \left( c_{1,2,m} \right) Y_1 \theta \phi_1 Y_1^{-m} \theta_2 \phi_2 + \frac{T^{(4)}(r_1, r_2)}{e_{r_1 r_2}} \sum_{m=-1}^{1} \alpha^{(4)} \left( c_{2,1,m} \right) Y_1 \theta \phi_1 Y_2^{-m} \theta_2 \phi_2,$$

where $\alpha^{(4)}(c_{1,2,m}) = -\pi^{-1} G_c(1, 2, m)$, $T^{(4)}(1,2,1) \in H_0^1(\Omega)$ solves

$$-\frac{1}{2} \Delta T^{(4)}(1,2,1) + (\kappa_2(r_1) + \kappa_1(r_2)) T^{(4)}(1,2,1) = r_1^3 r_2 e^{-r_1 - r_2} \quad \text{in } \Omega,$$

and $T^{(4)}(1,2,1) = T^{(4)}(2,1,1)$. A representation of $T^{(4)}(2,1,1)$ can be seen in Figure 1.

Computation of $\phi_5$. We have

$$B^{(5)} = r_1 r_2 \sum_{m=-1}^{1} G_c(1, 3, m) Y_1 \theta \phi_1 Y_3^{-m} \theta_2 \phi_2 + r_2^2 \sum_{m=-2}^{2} G_c(2, 2, m) Y_2 \theta \phi_1 Y_2^{-m} \theta_2 \phi_2$$

$$+ r_1^3 r_2^3 \sum_{m=-1}^{1} G_c(3, 1, m) Y_1 \theta \phi_1 Y_1^{-m} \theta_2 \phi_2,$$
and

\[ (H_0 - \lambda_0)\phi_5 = -B^{(5)}\phi_0, \]
\[ \langle \phi_0, \phi_5 \rangle = 0, \]

since \( \phi_1 = \phi_2 = 0 \) and \( C_k = 0 \) for \( 1 \leq k \leq 5 \). We thus have \( \mathcal{L}_5 = \{(1, 3), (2, 2), (3, 1)\} \) and

\[
\psi^{(5)} = \frac{T^{(5)}_{(1,3)}(r_1, r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha^{(5)}_{(1,3,m)} Y_1^m(\theta_1, \phi_1) Y_3^{-m}(\theta_2, \phi_2) \\
+ \frac{T^{(5)}_{(2,2)}(r_1, r_2)}{r_1 r_2} \sum_{m=-2}^{2} \alpha^{(5)}_{(2,2,m)} Y_2^m(\theta_1, \phi_1) Y_2^{-m}(\theta_2, \phi_2) \\
+ \frac{T^{(5)}_{(3,1)}(r_1, r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha^{(5)}_{(3,1,m)} Y_3^m(\theta_1, \phi_1) Y_1^{-m}(\theta_2, \phi_2),
\]

where \( \alpha^{(5)}_{(l_1,l_2,m)} = -\pi^{-1}G_c(l_1, l_2, m), T^{(5)}_{(l_1,3)} \in H^1_0(\Omega) \) solves

\[
-\frac{1}{2} \Delta_2 T^{(5)}_{(1,3)}(r_1, r_2) + (\kappa_1(r_1) + \kappa_3(r_2)) T^{(5)}_{(1,3)} = r_1^2 r_2^4 e^{-(r_1+r_2)},
\]

\( T^{(5)}_{(2,2)} \in H^1_0(\Omega) \) solves

\[
-\frac{1}{2} \Delta_2 T^{(5)}_{(2,2)}(r_1, r_2) + (\kappa_2(r_1) + \kappa_2(r_2)) T^{(5)}_{(2,2)} = r_1^3 r_2^3 e^{-(r_1+r_2)},
\]

and \( T^{(5)}_{(3,1)}(r_1, r_2) = T^{(5)}_{(1,3)}(r_2, r_1) \).

**Computation of \( \lambda_n \) for \( 6 \leq n \leq 11 \).** From (30) and the fact that \( C_n = 0 \) for \( 3 \leq n \leq 5 \), we
obtain, using (31), (38), (39), Table 1, and the symmetries of the coefficients \( \beta_{(i_1, l_2)}^{(3)} \) and \( t_{(i_1, l_2)}^{(3)} \),

\[
C_6 = -\langle \phi_0, B^{(3)} \phi_3 \rangle = \beta_{(1, 1)}^{(3)} t_{(1, 1)}^{(3)},
\]

\[
C_7 = -\langle \phi_0, B^{(3)} \phi_4 \rangle - \langle \phi_0, B^{(4)} \phi_3 \rangle = 0,
\]

\[
C_8 = -\langle \phi_0, B^{(3)} \phi_5 \rangle - \langle \phi_0, B^{(4)} \phi_4 \rangle - \langle \phi_0, B^{(5)} \phi_3 \rangle = -\langle \phi_0, B^{(4)} \phi_4 \rangle
\]

\[
= \beta_{(1, 2)}^{(4)} t_{(1, 2)}^{(4)} + \beta_{(2, 1)}^{(4)} t_{(2, 1)}^{(4)} = 2 \beta_{(1, 2)}^{(4)} t_{(1, 2)}^{(4)},
\]

\[
C_9 = -\langle \phi_0, B^{(3)} \phi_6 \rangle - \langle \phi_0, B^{(4)} \phi_5 \rangle - \langle \phi_0, B^{(5)} \phi_4 \rangle - \langle \phi_0, B^{(6)} \phi_3 \rangle = C_6 \langle \phi_0, \phi_3 \rangle = 0,
\]

\[
C_{10} = -\sum_{k=3}^{7} \langle \phi_0, B^{(k)} \phi_{10-k} \rangle - \sum_{k=6}^{7} C_k \langle \phi_0, \phi_{10-k} \rangle = -\langle \phi_0, B^{(5)} \phi_5 \rangle
\]

\[
= \beta_{(1, 3)}^{(5)} t_{(1, 3)}^{(5)} + \beta_{(2, 2)}^{(5)} t_{(2, 2)}^{(5)} + \beta_{(3, 1)}^{(5)} t_{(3, 1)}^{(5)} = 2 \beta_{(1, 3)}^{(5)} t_{(1, 3)}^{(5)} + \beta_{(2, 2)}^{(5)} t_{(2, 2)}^{(5)},
\]

\[
C_{11} = -\sum_{k=3}^{8} \langle \phi_0, B^{(k)} \phi_{11-k} \rangle - \sum_{k=6}^{8} C_k \langle \phi_0, \phi_{11-k} \rangle = -\langle \phi_0, B^{(4)} \phi_7 \rangle - \langle \phi_0, B^{(5)} \phi_6 \rangle
\]

\[
= \beta_{(1, 2)}^{(7)} t_{(1, 2)}^{(7)} + \beta_{(2, 1)}^{(7)} t_{(2, 1)}^{(7)} + \beta_{(2, 2)}^{(6)} t_{(2, 2)}^{(6)},
\]

As \( c_{(i_1, l_2, m)}^{(n)} = -\pi^{-1} G(l_1, l_2, m) \) for \( n = 3, 4, 5 \), \( (l_1, l_2) \in \mathcal{L}_n \) and \( -\min(l_1, l_2) \leq m \leq \min(l_1, l_2), \)

we obtain, using (17), that

\[
(\alpha_{(i_1, l_2, m)}^{(n)})^2 = \frac{16 ((l_1 + l_2)!)^2}{(2l_1 + 1)(2l_2 + 1)(l_1 - m)!l_1!m!(l_2 - m)!l_2!m!},
\]

and therefore

\[
\beta_{(1, 1)}^{(3)} = \sum_{m=-1}^{1} (\alpha_{(1,1,m)}^{(3)})^2 = \frac{16}{9} + \frac{64}{9} + \frac{16}{9} = \frac{32}{3},
\]

\[
\beta_{(1, 2)}^{(4)} = \sum_{m=-1}^{1} (\alpha_{(1,2,m)}^{(4)})^2 = \frac{16}{5} + \frac{3}{5} \times \frac{16}{5} + \frac{16}{5} = 16,
\]

\[
\beta_{(1, 3)}^{(5)} = \sum_{m=-1}^{1} (\alpha_{(1,3,m)}^{(5)})^2 = \frac{64}{3}, \quad \beta_{(2, 2)}^{(6)} = \sum_{m=-2}^{2} (\alpha_{(2,2,m)}^{(6)})^2 = \frac{224}{5},
\]

so that

\[
C_6 = \frac{32}{3} \beta_{(1, 1)}^{(3)}, \quad C_7 = 0, \quad C_8 = 32 \beta_{(1, 2)}^{(4)}, \quad C_9 = 0, \quad C_{10} = \frac{128}{3} \beta_{(1, 3)}^{(5)} + \frac{224}{5} \beta_{(2, 2)}^{(6)}.
\]

It is optimal to use (51) to compute \( C_6, C_8, C_{10} \) since only \( \phi_n \) is needed to compute \( C_{2n} \). On the other hand, computing \( C_{11} \) using (50) requires computing \( \phi_6 \) and \( \phi_7 \), and it is therefore preferable to use Wigner’s \((2n+1)\) rule that allows computing \( C_{11} \) from \( \phi_3, \phi_4 \) and \( \phi_5 \).

**Computation of higher-order terms.** For \( n \geq 6 \), the right-hand side of (9) contains terms of the form \( B^{(k)} \phi_{n-k} \) with \( k \geq 3 \) and \( n - k \geq 1 \). The computation of \( \phi_n \) therefore requires solving 2D boundary value problems of the form

\[
-\frac{1}{2} \Delta T + (\kappa_{l_1}(r_1) + \kappa_{l_2}(r_2)) T = t_{l_1}' t_{l_2}' T^{(n-k)}(l_1', l_2')
\]

for some \( (l_1, l_2) \in \mathcal{L}_n, l_1' + l_2' = k - 1 \) and \( (l_1'', l_2'') \in \mathcal{L}_{n-k} \). The right-hand side of this equation is not explicit, but the above equation can nevertheless be solved numerically since \( T^{(n-k)}(l_1', l_2') \) has been previously computed numerically during the calculation of \( \phi_{n-k} \).

## 3 Numerical results

### 3.1 Comparison between different approaches

The following tables contain the results of the approximated values of the \( C_n \) coefficients computed by Ovsianikov and Mitroy [21], by Choy [12], by Pauling and Beach [22], and by the techniques
described in this paper. The latter consist in solving recursively the Modified Slater–Kirkwood boundary value problems of type (9) using a Galerkin scheme in finite-dimensional approximation spaces constructed from tensor products of 1D Laguerre functions with degrees lower of equal to $k$. With basic double-precision floating-point arithmetics, the latter approach is numerical stable up to $k = 11$ and provides results with excellent precision (relative error lower than $10^{-9}$). It is well-known that the conditioning of spectral methods for PDEs using orthogonal polynomial spaces grows exponentially. However, in the present case, the entries of the Galerkin matrix are square roots of rational numbers so that arbitrary precision can be obtained using symbolic computation. The method of Choy [12] is based on the Slater–Kirkwood algorithm [26], whereas the method of Pauling and Beach [22] is different. Although Slater and Kirkwood are referenced in [22], Pauling and Beach were motivated by a method of S. C. Wang [31].

| Method | $C_6$          | $C_8$          | $C_{10}$         | $C_{11}$         |
|--------|----------------|----------------|------------------|------------------|
| [22]   | 6.49903        | 124.399        | 1135.21          |                  |
| [12]   | 6.4990267      | 124.3990835    | 1135.2140398     |                  |
| This work | 6.49902670540  | 124.399083     | 3285.82841       | -3474.89803      |
| [21]   | 6.499026705406 | 124.3990835836| 3285.828414967   | -3474.898037882  |

Table 2: Comparison of the coefficients $C_6$ to $C_{11}$ between various papers and the basis states method and our method based on numerical solutions of boundary value problems of type (19) in tensor products of Laguerre functions up to degree 11 (for which round-off error is suitably controlled). These results agree at least to 9 digits with the results in [11, 20, 21, 27, 32].

The discrepancy between the Choy and Pauling–Beach results (who agree to the digits given) and the other methods for $C_{10}$ has the following origin. According to (49), we have

$$C_{10} = 2\beta^{(5)}_{(1,3)}t^{(5)}_{(1,3)} + \beta^{(5)}_{(2,2)}t^{(5)}_{(2,2)}.$$  

It appears that Choy in [12], who also was guided by [26], only computed the second term

$$\beta^{(5)}_{(2,2)}t^{(5)}_{(2,2)} = 1135.214\ldots$$  \hspace{1cm} (52)

| Method | $C_{12}$        | $C_{13}$        | $C_{14}$        | $C_{15}$        |
|--------|-----------------|-----------------|-----------------|-----------------|
| This work | 122727.608      | -326986.924     | 6361736.04      | -28395580.6     |
| [21]   | 122727.6087007  | -326986.9240441 | 6361736.045092  | -28395580.6     |

Table 3: Comparison of the $C_n$ coefficients $C_{12}$ to $C_{15}$ between [21] and our method based on numerical solutions of boundary value problems of type (19) in tensor products of Laguerre functions up to degree 11 (for which round-off error is suitably controlled). These results agree at least to 9 digits with the results in [20, 21, 32] for $C_{13}$ and $C_{15}$ and [20, 21] for $C_{12}$ and $C_{14}$.

| Method | $C_{16}$      | $C_{17} \times 10^{-9}$ | $C_{18} \times 10^{-10}$ | $C_{19} \times 10^{-11}$ |
|--------|---------------|--------------------------|---------------------------|--------------------------|
| This work | 441205192     | -2.73928165              | 3.93524773                | -3.07082459              |
| [21]   | 441205192.2739| -2.739281653140         | 3.93524773346             | -3.07082459389           |

Table 4: Comparison of the $C_n$ coefficients $C_{16}$ to $C_{19}$ between [21] and our method based on numerical solutions of boundary value problems of type (19) in tensor products of Laguerre functions up to degree 11 (for which round-off error is suitably controlled). These results agree at least to 9 digits with the results in [20, 21].
3.2 Role of continuous spectra in sum-over-state formulae

It follows from (41), (42) and (48) that the leading coefficient \( C_6 \) of the van der Waals expansion can be written as

\[
C_6 = \langle \mathcal{B}^{(3)} \phi_0, (H_0 - \lambda_0)^{-1} \mathcal{B}^{(3)} \phi_0 \rangle,
\]

where \((H_0 - \lambda_0)^{-1}\) is the inverse of the restriction to \( H_0 - \lambda_0 \) to the invariant subspace \( \phi_0 \) (which is well-defined since \( \lambda_0 \) is a non-degenerate eigenvalue of the self-adjoint operator \( H_0 \)). This expression is sometimes wrongly rewritten as a sum-over-state formula

\[
C_6 = \sum_j \frac{|\langle \psi_j, \mathcal{B}^{(3)} \phi_0 \rangle|^2}{E_j - E_0} \quad \text{(wrong),}
\]

with \( \psi_0 := \phi_0, E_0 := \lambda_0 = -1 \), where the \( \psi_j \)'s form an orthonormal family of excited states of \( H_0 \) associated with the eigenvalues \( E_j \). This is not possible because \( H_0 \) has a non-empty continuous spectrum. Using (53) with a sum running over the excited states of \( H_0 \) (and omitting an integral over the scattering states of \( H_0 \)) leads to an error that we are going to estimate. We have

\[
C_6' := \sum_j \frac{|\langle \psi_j, \mathcal{B}^{(3)} \phi_0 \rangle|^2}{E_j - E_0} = -\langle \mathcal{B}^{(3)} \phi_0, \phi_{3,pp} \rangle,
\]

where \( \phi_{3,pp} \) is the projection of \( \phi_3 \) on the Hilbert space spanned by the eigenfunctions of \( H_0 \). Recall that the eigenvalues and associated eigenfunctions of the hydrogen atom Hamiltonian \( h_0 := -\frac{\hbar^2}{2\mu} \Delta - \frac{e^2}{4\pi\epsilon r} \), which is a self-adjoint operator on \( L^2(\mathbb{R}^3) \), are of the form

\[
\varepsilon_n = -\frac{1}{2n^2}; \quad \psi_{n,l,m}(r) = \varphi_{n,l}(r) Y_l^m(\theta, \phi), \quad n \in \mathbb{N}^+, \quad 0 \leq l \leq n - 1, \quad -l \leq m \leq l,
\]

with

\[
\varphi_{n,1} = \sqrt{\frac{2}{n}} \frac{(n - 2)!}{2n(n + 1)!} \left( \frac{2r}{n} \right)^{n/2} L_{n-2}^{(3)} \left( \frac{2r}{n} \right) e^{-r/n},
\]

where the associated Laguerre polynomials of the second type \( L_n^{(m)} \), \( n, m \in \mathbb{N} \), are defined from the Laguerre polynomial \( L_n \) and are given by

\[
L_n^{(m)}(x) = (-1)^m \frac{d^m}{dx^m} L_{n+m}(x) = \frac{1}{n!} \sum_{k=0}^n \frac{n!}{k!(n-k)!} \left( \frac{m+n}{n-k} \right) (-x)^k.
\]

The eigenvalues and associated eigenfunctions of \( H_0 \) are therefore given by

\[
\varepsilon_{n_1, n_2} = \varepsilon_{n_1} + \varepsilon_{n_2} = -\frac{1}{2n_1^2} - \frac{1}{2n_2^2}; \quad \Psi_{n_1,l_1,m_1;n_2,l_2,m_2} = \psi_{n_1,l_1,m_1} \otimes \psi_{n_2,l_2,m_2},
\]

for \( n_j \in \mathbb{N}^+, 0 \leq l_j \leq n_j - 1, \quad -l_j \leq m_j \leq l_j \). Note that \( \phi_0 = \Psi_{1,0,0,1,0,0} \). We therefore have

\[
C_6' = \sum_{(n_1,n_2) \in (\mathbb{N}^+)^2} \sum_{l_1} \sum_{l_2} \sum_{m_1} \sum_{m_2} \frac{|\langle \Psi_{n_1,l_1,m_1;n_2,l_2,m_2}, \mathcal{B}^{(3)} \phi_0 \rangle|^2}{\varepsilon_{n_1} + \varepsilon_{n_2} + 1},
\]

Using (40) and the \( L^2(S^2) \)-orthonormality of the spherical harmonics, we get

\[
\langle \Psi_{n_1,l_1,m_1;n_2,l_2,m_2}, \mathcal{B}^{(3)} \phi_0 \rangle = \pi^{-1} S_{n_1} S_{n_2} \sum_{m=-1}^{1} G_c(1,1,m) \delta_{l_1} \delta_{l_2} \delta_{m_1} \delta_{m_2},
\]

where

\[
S_n := \int_0^{+\infty} r^3 e^{-r} \varphi_{n,1}(r) \, dr = 8n^3 \frac{(n-1)^{n-3}}{(n+1)^{n+3}} \sqrt{\frac{(n+1)!}{(n-2)!}}
\]
The latter expression is derived in Appendix C. We finally obtain

\[
C'_6 = \pi^{-2} \sum_{m=-1}^{1} |G_c(1,1,m)|^2 \sum_{n_1,n_2 \geq 2} \frac{S_{n_1}^2 S_{n_2}^2}{1 - \frac{4n_1}{2n_1^2} - \frac{4n_2}{2n_2^2}} = \frac{32}{3} \sum_{n_1,n_2 \geq 2} \frac{S_{n_1}^2 S_{n_2}^2}{1 - \frac{4n_1}{2n_1^2} - \frac{4n_2}{2n_2^2}}.
\]

(58)

Summing up the terms of the above series for \( n_1, n_2 \leq 300 \) (note that \( S_n \sim n \to \infty \frac{8}{\pi n^{3/2}} \)), we obtain the approximate value

\[
C'_6 \simeq 3.923
\]

which shows that the continuous spectrum plays a major role in the sum-over-state evaluation of the \( C_6 \) coefficient of the hydrogen molecule (recall that \( C_6 \simeq 6.499 \)).

4 Proofs

We now establish the results stated above, starting from Lemma 4.

4.1 Proof of Lemma 4

Recall that the Hydrogen atom Hamiltonian \( h_0 = -\frac{1}{2} \Delta - \frac{1}{r^2} \) introduced in the previous section is a self-adjoint operator on \( L^2(\mathbb{R}^3) \) with domain \( H^2(\mathbb{R}^3) \), and that its ground state is non-degenerate:

\[
h_0 \psi_{1.0.0} = -\frac{1}{2} \psi_{1.0.0} \quad \text{with} \quad \psi_{1.0.0} = \varphi_{1.0}(r) Y_0^0(\theta, \phi) = \pi^{-1/2} e^{-r}, \quad \| \psi_{1.0.0} \|_{L^2(\mathbb{R}^3)} = 1.
\]

Since \( H_0 = h_0 \otimes 1_{L^2(\mathbb{R}^3)} + 1_{L^2(\mathbb{R}^3)} \otimes h_0 \), \( H_0 \) is a self-adjoint operator on \( L^2(\mathbb{R}^3 \times \mathbb{R}^3) \) with domain \( H^2(\mathbb{R}^3 \times \mathbb{R}^3) \) and it also has a non-degenerate ground state

\[
H_0 \phi_0 = \lambda_0 \phi_0 \quad \text{with} \quad \phi_0 = \psi_{1.0.0} \otimes \psi_{1.0.0} = \pi^{-1} e^{-(r_1 + r_2)}, \quad \| \phi_0 \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1 \quad \text{and} \quad \lambda_0 = -1.
\]

Given \((\alpha, F) \in \mathbb{R} \times L^2(\mathbb{R}^3 \times \mathbb{R}^3)\), the problem consisting of seeking \((\mu, \Psi) \in \mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3)\) such that

\[
(H_0 - \lambda_0) \Psi = F - \mu \phi_0, \quad \langle \phi_0, \Psi \rangle = \alpha,
\]

(59)

is well-posed and its unique solution is given

\[
\Psi = (H_0 - \lambda_0)^{-1} \phi_0 F + \alpha \phi_0, \quad \mu = \langle \phi_0, F \rangle,
\]

where \((H_0 - \lambda_0)^{-1}\phi_0\) is the inverse of \(H_0 - \lambda_0\) on the invariant subspace \(\phi_0^\perp\) and \(\Pi_{\phi_0^\perp} F := F - \langle \phi_0, F \rangle \phi_0\) the orthogonal projection of \( F \) on \(\phi_0^\perp\). Consider the unitary map

\[
\mathcal{U} : L^2(\Omega) \otimes L^2(S^2) \otimes L^2(S^2) \to L^2(\mathbb{R}^3 \times \mathbb{R}^3) \equiv L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)
\]

induced by the spherical coordinates defined for all \( f \in L^2(\Omega), l_1, l_2 \in \mathbb{N}, -l_j \leq m_j \leq l_j \) by

\[
(\mathcal{U}(f \otimes s_1 \otimes s_2))(r_1, r_2) = \frac{f(r_1, |r_2|)}{|r_1| |r_2|} s_1 \left( \frac{r_1}{|r_1|} \right) s_2 \left( \frac{r_2}{|r_2|} \right).
\]

Since \((Y^m_t)_{t \in \mathbb{N}, -t \leq m \leq t}\) is an orthonormal basis of \(L^2(S^2)\), we have

\[
L^2(\Omega) \otimes L^2(S^2) \otimes L^2(S^2) = \bigoplus_{l_1,l_2 \in \mathbb{N}} \bigoplus_{m_1=-l_1}^{l_1} \bigoplus_{m_2=-l_2}^{l_2} H^m_{l_1,l_2}
\]

where \(H^m_{l_1,l_2} := L^2(\Omega) \otimes CY^m_{l_1} \otimes CY^m_{l_2} \). It follows from classical results for Schrödinger operators on \(L^2(\mathbb{R}^3)\) with central potentials (see e.g. [23, Section XIII.3.B]) that each \(H^m_{l_1,l_2}\) is an invariant subspace for \(\mathcal{U}^* H_0 \mathcal{U} \) and that

\[
\mathcal{U}^* H_0 \mathcal{U}|_{H^m_{l_1,l_2}} = H_{l_1,l_2} \otimes 1_{CY^m_{l_1}} \otimes 1_{CY^m_{l_2}}.
\]
that \( \leq \tilde{\alpha} \) in (19) can be dealt with similarly, by replacing \( H_0 \) with \( H_1 \).

Choosing \( \alpha \) where the expression of \( H_{1,t_2} \) can be derived by adapted the arguments in [10, Section 3], that we do not detail here for the sake of brevity: \( H_{1,t_2} \) is the self-adjoint operator on \( L^2(\Omega) \) with form domain \( H^1_0(\Omega) \) defined by

\[
H_{1,t_2} = -\frac{1}{2} \Delta + \kappa_{t_1}(r_1) + \kappa_{t_2}(r_2) + \lambda_0.
\]  

(60)

Note that the operator \( H_{1,t_2} \) on \( L^2(\Omega) = L^2(0, +\infty) \otimes L^2(0, +\infty) \) can itself be decomposed as

\[
H_{1,t_2} = h_1 \otimes 1_{L^2(0, +\infty)} + 1_{L^2(0, +\infty)} \otimes h_2 \geq -\frac{1}{2(l_1 + 1)^2} - \frac{1}{2(l_2 + 1)^2},
\]

where for each \( l \in \mathbb{N} \), \( h_l \) is the self-adjoint operator on \( L^2(0, +\infty) \) with form domain \( H^1_0(0, +\infty) \) defined by

\[
h_l := -\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} = -\frac{d^2}{dr^2} + \kappa_l - \frac{1}{r}.
\]

This well-known operator allows one to construct the bound-states of hydrogen atom with orbital quantum number \( l \). It satisfies \( h_l \geq -\frac{1}{2(l+1)^2} \) and its ground state eigenvalue \(-\frac{1}{2(l+1)^2}\) is non-degenerate. It follows from this bound that

\[
H_{1,t_2} - \lambda_0 = H_{1,t_2} + 1 \geq \frac{3}{8} \text{ for all } (l_1, l_2) \in \mathbb{N}^2 \setminus \{(0,0)\}.
\]

(61)

Choosing \( \alpha = 0 \) in (59) amounts to enforcing that the solution \( \Psi \) is in \( \phi_0^1 \). Taking \( \alpha = 0 \) and

\[
F = \iota_{(r_1,r_2)}^1 \cdot Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) = \mathcal{U}(f \otimes Y_{l_1}^{m_1} \otimes Y_{l_2}^{m_2}),
\]

with \( f \in L^2(\Omega) \), it follows that (21) has a unique solution in \( H^2(\mathbb{R}^2) \) if and only if \( \mu = \langle \phi_0, F \rangle = 0 \), that is

\[
\delta_{(l_1, l_2) = (0,0)} f(r_1, r_2) e^{-(r_1 + r_2)} r_1 r_2 dr_1 dr_2 = 0,
\]

in which case the solution is given by \( \Psi = \mathcal{U}(T \otimes Y_{l_1}^{m_1} \otimes Y_{l_2}^{m_2}) \) where

\[
T := (H_{1,t_2} - \lambda_0)^{-1} f \quad \text{if} \quad (l_1, l_2) \neq (0,0),
\]

\[
T := (H_{0,0} - \lambda_0)^{-1} f \quad \text{if} \quad (l_1, l_2) = (0,0).
\]

We therefore have

\[
\psi = \frac{T(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2),
\]

where \( T \) is the unique solution to (19) in \( H^1_0(\Omega) \) if \( (l_1, l_2) \neq (0,0) \) and \( T \) is the unique solution to (19) in \( H^1_0(\Omega) = H^1_0(\Omega) \cap (r_1 r_2 e^{-(r_1 + r_2) - \frac{1}{2}} - \frac{1}{2}) - \frac{1}{2} \) - \frac{1}{2} \) if \( (l_1, l_2) = (0,0) \).

The fact that if \( f \) decays exponentially at infinity, then so does \( T \), hence \( \psi \), is a consequence of the following result, whose proof follows the same lines as in [10, Section 3.3] where this result is established for the special case when \( (l_1, l_2) = (1,1) \) and \( f = r_1 r_2 e^{-(r_1 + r_2)} \).

**Lemma 6.** If the function \( f \) of (19) decays exponentially at infinity at a rate \( \eta > 0 \), in the sense that

\[
\|e^{\|\eta(r_1 + r_2)f\|_{L^2(\Omega)}} < \infty,
\]

then the unique solution \( T \) of (19) also decays exponentially at infinity. More precisely, for all \( 0 < \alpha < \sqrt{3}/8 \), there exists a constant \( C_\alpha \in \mathbb{R}_+ \) such that for all \( \eta > \alpha \) and all \( f \in L^2(\Omega) \) satisfying (62), it holds

\[
\|e^{\alpha(r_1 + r_2)T}\|_{H^1(\Omega)} \leq C_\alpha \|e^{\eta(r_1 + r_2)f}\|_{L^2(\Omega)}.
\]

(63)

**Proof.** We limit ourselves to the case when \( (l_1, l_2) \neq (0,0) \). The special case \( (l_1, l_2) = (0,0) \) can be dealt with similarly, by replacing \( H^1_0(\Omega) \) by \( H^1_0(\Omega) \). Let \( a \) be the continuous bilinear form on \( H^1_0(\Omega) \) associated with the positive self-adjoint operator \( H_{0,1} - \lambda_0 \):

\[
\forall u, v \in H^1_0(\Omega), \quad a(u, v) = \frac{1}{2} \int_{\Omega} \nabla u \cdot \nabla v + \int_{\Omega} (\kappa_{t_1}(r_1) + \kappa_{t_2}(r_2))u(r_1, r_2)v(r_1, r_2) dr_1 dr_2.
\]
Recall that the continuity of \( a \) can be shown directly (without using the fact that \( H^1_0(\Omega) \) is the form domain of \( H_{01}^{1/2} \)) as a straightforward consequence of the one-dimensional Hardy inequality

\[
\forall g \in H^1_0(0, +\infty), \quad \int_0^\infty (g(r)/r)dr \leq 4 \int_0^\infty g'(r)^2 dr.
\] (64)

It follows from (61) that \( a \geq \frac{1}{2} \) (in the sense of quadratic forms on \( L^2(\Omega) \)). For \( 0 \leq \alpha < \sqrt{3/8} \), we introduce the continuous bilinear form \( a_\alpha \) on \( H^1_0(\Omega) \times H^1_0(\Omega) \) defined by

\[
\forall u, v \in H^1_0(\Omega), \quad a_\alpha(u, v) = a(u, v) - \int_\Omega a_2(u) \frac{\partial v}{\partial r_1}(r) + \frac{\partial v}{\partial r_2}(r) \, dr - \int_\Omega a_2 u(r) v(r) \, dr,
\]

for which

\[
\forall v \in H^1_0(\Omega), \quad a_\alpha(v, v) = a(v, v) - \alpha^2 \|v\|^2_{L^2(\Omega)} \geq \left( \frac{3}{8} - \alpha^2 \right) \|v\|^2_{L^2(\Omega)} > 0.
\]

Using either the fact that \( \kappa_l(r) \geq \frac{1}{4} \) (for \( l \geq 1 \)) or the Hardy inequality (64) (for \( l = 0 \)), we also have

\[
\forall v \in H^1_0(\Omega), \quad a_\alpha(v, v) = a(v, v) - \alpha^2 \|v\|^2_{L^2(\Omega)} \geq \frac{1}{4} \int_\Omega |\nabla v|^2 - 2\|v\|^2_{L^2}.
\]

Since \( a \geq \frac{1}{8} \) and \( \alpha \geq \left( \frac{3}{8} - \alpha^2 \right) > 0 \), the above bound implies that \( a \) and \( a_\alpha \) are both continuous and coercive on \( H^1_0(\Omega) \). The function \( T \in H^1_0(\Omega) \) solution to (19) is also the unique solution to the variational equation

\[
\forall w \in H^1_0(\Omega), \quad a(T, w) = \int_\Omega f w.
\]

Proceeding as in [10, Section 3.3], we obtain that for all \( u \in H^1_0(\Omega) \) such that \( e^{a(r_1 + r_2)} u \in H^1_0(\Omega) \) and \( w \in C^\infty_c(\Omega) \), we have

\[
a_\alpha(e^{a(r_1 + r_2)} u, w) = a(u, e^{a(r_1 + r_2)} w).
\] (65)

Consider now \( f \in L^2(\Omega) \) satisfying (62) for some \( \eta > \alpha \). The function \( e^{\alpha(r_1 + r_2)} f \) is in \( L^2(\Omega) \), so that the problem of finding \( v \in H^1(\Omega) \) such that

\[
\forall w \in H^1_0(\Omega), \quad a_\alpha(v, w) = \int_\Omega e^{\alpha(r_1 + r_2)} f w
\]

has a unique solution \( v \), satisfying \( \|v\|_{H^1(\Omega)} \leq C_\alpha \|e^{\alpha(r_1 + r_2)} f\|_{L^2(\Omega)} \leq C_\alpha \|e^{\eta(r_1 + r_2)} f\|_{L^2(\Omega)} \), where \( C_\alpha \geq 1 \) is the ratio between the continuity constant and the coercivity constant of \( a_\alpha \). Let \( u = e^{-\alpha(r_1 + r_2)} v \in H^1_0(\Omega) \). In view of (65), we have

\[
\forall w \in C^\infty_c(\Omega), \quad a(u, e^{\alpha(r_1 + r_2)} w) = a_\alpha(v, w) = \int_\Omega e^{\alpha(r_1 + r_2)} f w = a(T, e^{\alpha(r_1 + r_2)} w).
\]

Hence, \( T = u \) and \( \|e^{\alpha(r_1 + r_2)} T\|_{H^1(\Omega)} = \|e^{\alpha(r_1 + r_2)} u\|_{H^1(\Omega)} = \|v\|_{H^1(\Omega)} \leq C_\alpha \|e^{\eta(r_1 + r_2)} f\|_{L^2(\Omega)} \). \( \square \)

As a consequence, we have

\[
\|e^{\alpha(r_1 + r_2)} \psi\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = \|e^{\alpha(r_1 + r_2)} T\|_{L^2(\Omega)} \leq \|e^{\alpha(r_1 + r_2)} T\|_{H^1(\Omega)} \leq C_\alpha \|e^{\eta(r_1 + r_2)} f\|_{L^2(\mathbb{R}^3)},
\]

which proves (25). In addition, a simple calculation using (64) shows that for all \( g \in H^1_0(\Omega) \)

\[
\left\| \frac{g}{r_1 r_2} \otimes \frac{r_1 m_1}{l_1} \otimes r_2 \otimes r_2 \right\|_{H^1_0(\mathbb{R}^3 \times \mathbb{R}^3)} \leq \|g\|^2_{H^1(\Omega)} + l_1(l_1 + 1) \left| \frac{g}{r_1} \right|^2_{L^2(\Omega)} + l_2(l_2 + 1) \left| \frac{g}{r_2} \right|^2_{L^2(\Omega)} \leq \left( 1 + 4l_1(l_1 + 1) + 4l_2(l_2 + 1) \right) \|g\|^2_{H^1},
\]

yielding

\[
\|e^{\alpha(r_1 + r_2)} \psi\|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq \left( 1 + 4l_1(l_1 + 1) + 4l_2(l_2 + 1) \right)^{1/2} \|e^{\alpha(r_1 + r_2)} T\|_{H^1(\Omega)} \leq C_\alpha \left( 1 + 4l_1(l_1 + 1) + 4l_2(l_2 + 1) \right)^{1/2} \|e^{\eta(r_1 + r_2)} f\|_{L^2(\mathbb{R}^3)}. \]

Lastly, since \( H_{1,2} \) is a real operator in the sense that \( \overline{H_{1,2} \phi} = H_{1,2} \phi \) for all \( \phi \in D(H_{1,2}) \), it is obvious that \( T \) is real-valued, whenever \( f \) is.
4.2 Proof of Lemma 1 and Theorem 5

We have seen in the previous section that for each \((\alpha, F) \in \mathbb{R} \times L^2(\mathbb{R}^3 \times \mathbb{R}^3), (59)\) has a unique solution \((\mu, \psi) \in \mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3). \) For \(n = 1,\) we have
\[
(H_0 - \lambda_0)\phi_1 = -C_1\phi_0, \quad \langle \phi_0, \phi_1 \rangle = 0,
\]
and it is clear that \((C_1, \phi_1) = (0, 0)\) is a solution, hence the solution, to this system. Likewise, for \(n = 2,\) we have
\[
(H_0 - \lambda_0)\phi_2 = -C_1\phi_1 - C_2\phi_0 = -C_2\phi_2, \quad \langle \phi_0, \phi_2 \rangle = -\frac{1}{2}\langle \phi_1, \phi_1 \rangle = 0,
\]
so that \((C_2, \phi_2) = (0, 0).\) To prove that the Rayleigh–Schrödinger triangular system (9)-(10) is well-posed and that \(\phi_n\) is of the form (26), we proceed by induction on \(n.\) It is proven in [10] that for \(n = 3,\)
\[
\phi_3 = \frac{T^{(3)}(r_1, r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha^{(3)}_{(1,1,m)} Y^m_1(\theta_1, \phi_1) Y^{-m}_1(\theta_2, \phi_2),
\]
with \(\alpha^{(3)}_{(1,1,m)} = -\pi G_c(1, 1, m)\) and \(\|T^{(3)}(r_1, r_2) e^{\eta^{(r_2)}_1} \|_{H^1(\Omega)} = C_{1,1}^3 < \infty.\) Let \(\mathcal{L}_3 = \{(1, 1)\}\) and assume that for some \(n \geq 3\) the following recursion hypotheses are satisfied (this is the case for \(n = 3)\): for all \(3 \leq k \leq n,\)
\[
\phi_k = \sum_{(l_1, l_2) \in \mathcal{E}_k} T^{(k)}_{(l_1, l_2)}(r_1, r_2) \left( \sum_{m = -\min(l_1, l_2)}^{\min(l_1, l_2)} \alpha^{(k)}_{(l_1, l_2, m)} Y^m_{l_1}(\theta_1, \phi_1) Y^{-m}_{l_2}(\theta_2, \phi_2) \right),
\]
for some finite set \(\mathcal{E}_k \subset \mathbb{N}^2\) with cardinality \(N_k < \infty,\) where \(T^{(k)}_{(l_1, l_2)}\) is the unique solution to (19) in \(H^1(\Omega)\) (or in \(\bar{H}^1(\Omega)\) if \(l_1 = l_2 = 0\) for \(f = f^{(k)}_{(l_1, l_2)} \in L^2(\Omega)\) and that for all \((l_1, l_2) \in \mathcal{L}_k\) there exists \(\eta^{(r_1, r_2)}_{l_1, l_2} > 0\) such that
\[
\|T^{(k)}_{(l_1, l_2)}(r_1, r_2) e^{\eta^{(r_2)}_{l_1, l_2}} \|_{H^1(\Omega)} = C_{l_1, l_2}^k < \infty.
\]
From (14), the fact that \(\phi_1 = \phi_2 = 0\) and the recursion hypothesis (66), we obtain that for all \(3 \leq k \leq n + 1,\)
\[
\mathcal{B}^{(k)} \phi_{n+1-k} = \sum_{l_1, l_2 \in \mathcal{L}_{k-1}} \sum_{l'_1, l'_2 \in \mathcal{L}_{n-k}} \sum_{m = -\min(l_1, l_2)}^{\min(l_1, l_2)} \sum_{m' = -\min(l'_1, l'_2)}^{\min(l'_1, l'_2)} \mathcal{U} \left( f^{m,m'}_{n-k+1,l_1,l'_1,l_2,l'_2} \otimes Y^m_{l_1} Y^{m'}_{l'_1} \otimes Y^{-m}_{l_2} Y^{-m'}_{l'_2} \right),
\]
where
\[
f^{m,m'}_{l_1,l'_1,l_2,l'_2}(r_1, r_2) := G_c(l_1, l_2, m) r_1^{l_1} r_2^{l_2} \alpha^{(j)}_{(l_1, l'_1, l_2, l'_2)} T^{(j)}_{(l_1, l'_1)}(r_1, r_2).
\]
In addition, we have
\[
Y^m_l Y^{m'}_{l'} = \sum_{l'' = |l-l'|}^{l+l'} \zeta^{m,m'}_{l,l',l''} Y^{m+m'}_{l''} \quad \text{where} \quad \zeta^{m,m'}_{l,l',l''} = 0 \quad \text{if} \quad l + l' + l'' \notin 2\mathbb{N},
\]
where the coefficients \(\zeta^{m,m'}_{l,l',l''} \in \mathbb{R}\) can be computed explicitly using Wigner's 3-j symbols [9, p. 146]:
\[
\zeta^{m,m'}_{l,l',l''} = (-1)^{m+m'} \frac{\sqrt{(2l+1)(2l'+1)(2l''+1)}}{4\pi} \begin{pmatrix} l & l' & l'' \\ m & m' & -m-m' \end{pmatrix}.
\]
This implies that
\[
- \sum_{k=3}^{n+1} \mathcal{B}^{(k)} \phi_{n+1-k} - \sum_{k=1}^{n+1} C_k \phi_{n+1-k} = \sum_{(l_1, l_2) \in \mathcal{L}_{n+1}} \frac{f^{(n+1)}_{(l_1, l_2)}(r_1, r_2)}{r_1 r_2} \left( \sum_{m = -\min(l_1, l_2)}^{\min(l_1, l_2)} \alpha^{(k)}_{(l_1, l_2, m)} Y^m_{l_1}(\theta_1, \phi_1) Y^{-m}_{l_2}(\theta_2, \phi_2) \right),
\]
for some $\mathcal{L}_{n+1} \subset \mathbb{N}^2$ with finite cardinality, where the $f_{(l_1,l_2)}^{(n+1)}$'s are linear combinations of the functions $r_1^{(l_1,l_2)} \in L^2(\Omega)$, $3 \leq j \leq n$, $l_1', l_2' \in \mathcal{L}_j$, $l_1 + l_2 + j \leq n + 1$, and therefore satisfy in view of (67)
\[
\|f_{(l_1,l_2)}^{(n+1)}(r_1,r_2)e^{\eta_{l_1,l_2,r_1,r_2}}\|_{H^1(\Omega)} < \infty
\]
for some $\eta_{l_1,l_2} > 0$. Therefore the problem consisting in seeking $(C_{n+1},\phi_{n+1}) \in \mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3)$ satisfying
\[
(H_0 - \lambda_0)\phi_{n+1} = -\sum_{k=3}^{n+1} B^{(k)}(\phi_{n+1-k}, -\sum_{k=1}^{n+1} C_k \phi_{n+1-k}, \langle \phi_0, \phi_{n+1} \rangle = \frac{1}{2}\sum_{k=1}^{n} \langle \phi_k, \phi_{n+1-k} \rangle
\]
is well-posed and we deduce from Lemma 4 that
\[
\phi_{n+1} := \sum_{(l_1,l_2) \in \mathcal{L}_{n+1}} T_{(l_1,l_2)}^{(n+1)}(r_1, r_2) \left( \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \alpha^{(l_1,l_2,m)} T_{(l_1,l_2,m)}^{(n+1)}(\phi_0) \right),
\]
where $T_{(l_1,l_2)}^{(n+1)}$ is the unique solution to (19) in $H^1(\Omega)$ (or in $\bar{H}^1(\Omega)$ if $l_1 = l_2 = 0$) for $f = f_{(l_1,l_2)}^{(n+1)}$. In addition, it follows from (71) that (67) holds true for $k = n + 1$. Therefore, the Rayleigh–Schrödinger triangular system (9)-(10) is well-posed and the $T_{(l_1,l_2)}^{(n+1)}$'s decay exponentially at infinity in the sense of (67). From (66) we obtain that for $\alpha_n = \min_{(l_1,l_2) \in \mathcal{L}_n}(\eta_{l_1,l_2}^n) > 0$, we have
\[
\|e^{\alpha_n(r_1 + r_2)}\|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C_n \sum_{(l_1,l_2) \in \mathcal{L}_n} \|e^{\alpha_n(r_1 + r_2)}T_{(l_1,l_2)}^{(n+1)}(\phi_0)\|_{H^1(\Omega)}
\]
\[
\leq C_n \sum_{(l_1,l_2) \in \mathcal{L}_n} \|e^{\eta_{l_1,l_2}^n(r_1 + r_2)}T_{(l_1,l_2)}^{(n+1)}(\phi_0)\|_{H^1(\Omega)} < \infty,
\]
for some $C_n \in \mathbb{R}^+$, so that $\phi_n$ decays exponentially at infinity in the sense of (28). Lastly, we infer from Wigner’s $(2n + 1)$ rule and the fact that $\phi_1 = \phi_2 = 0$, that $C_n = 0$ for $1 \leq n \leq 5$. This completes the proof of both Lemma 1 and Theorem 5.

Let us finally explain how to construct Table 1. We have already shown that $\mathcal{L}_3 = \{(1,1),\}$, and from (68)-(70) and the fact that $\phi_1 = \phi_2 = 0$, we see that
\[
\mathcal{L}_{n+1} \subset \left( \bigcup_{k=3}^{n-2} \mathcal{M}_{k,n+1-k} \right) \cup \mathcal{M}_{n+1,0} \cup \left( \bigcup_{3 \leq k \leq n-5} \bigcup_{C_{n+1-k} \neq 0} \mathcal{L}_k \right),
\]
where for $k, n \geq 3$,
\[
\mathcal{M}_{k,0} = \{ (l_1,l_2) \in \mathbb{N}^* \times \mathbb{N}^* \mid l_1 + l_2 = k - 1 \} = \{ (1,k-2), \cdots, (k-2,1) \},
\]
\[
\mathcal{M}_{k,n} = \{ (l_1,l_2) \in \mathbb{N} \times \mathbb{N} \mid \exists (l'_1,l'_2) \in \mathcal{M}_{k,0}, \exists (l''_1,l''_2) \in \mathcal{L}_n \text{ s.t.} \}
\]
\[
|l'_j - l''_j| \leq l_j \leq l'_j + l''_j, l_j + l'_j + l''_j \in 2\mathbb{N}, j = 1,2.
\]

Consequently, we have
\[
\mathcal{L}_4 = \mathcal{M}_{4,0};
\]
\[
\mathcal{L}_5 = \mathcal{M}_{5,0};
\]
\[
\mathcal{L}_6 = \mathcal{M}_{3,3} \cup \mathcal{M}_{6,0} \quad \text{with} \quad \mathcal{M}_{3,3} = \{(0,2;0,2)\};
\]
\[
\mathcal{L}_7 = \mathcal{M}_{3,4} \cup \mathcal{M}_{4,3} \cup \mathcal{M}_{7,0} \quad \text{with} \quad \mathcal{M}_{3,4} = \mathcal{M}_{4,3} = \{(0,2;1,3),(1,3;0,2)\};
\]
\[
\mathcal{L}_8 = \mathcal{M}_{3,5} \cup \mathcal{M}_{4,4} \cup \mathcal{M}_{5,3} \cup \mathcal{M}_{8,0} \quad \text{with} \quad \mathcal{M}_{3,5} = \mathcal{M}_{5,3} = \{(0,2;2,4),(1,3;1,3),(2,4;0,2)\},
\]
\[
\mathcal{M}_{4,4} = \{(0,2;0,2),(0,2;4;0,2),(1,3;1,3)\}
\]
\[
\mathcal{L}_9 = \mathcal{M}_{3,6} \cup \mathcal{M}_{4,5} \cup \mathcal{M}_{5,4} \cup \mathcal{M}_{6,3} \cup \mathcal{M}_{9,0} \cup \mathcal{L}_3 \quad \text{with} \quad \mathcal{M}_{6,3} \subseteq \mathcal{M}_{4,6} = \{(0,2;3,5),(1,3;2,4),(2,4;1,3),(3,5;0,2),(1,3;1,3)\},
\]
\[
\mathcal{M}_{4,5} = \mathcal{M}_{5,4} = \{(0,2;1,3,5),(1,3;0,2,4),(2,4;1,3),(1,3;2,4),(0,2;4;1,3),(1,3;5;0,2)\},
\]
where we recall that $(l_1,l'_1;l_2,l''_2)$ (resp. $(l_1,l'_1;l_2,l''_2)$, $(l_1,l'_1,l''_1;l_2,l''_2)$) stands for the four (resp. six) pairs $(l_1,l_2)$, $(l_1',l_2)$, $(l_1',l_2')$, etc. After eliminating redundancies, we obtain Table 1.
4.3 Proof of Theorem 2

As in [10], we introduce the space
\[ \mathcal{V} = \left\{ v \in L^2(\mathbb{R}^3 \times \mathbb{R}^3) : v(r_1, r_2) = v(r_2, r_1) \ \forall r_1, r_2 \in \mathbb{R}^3 \right\}, \] (72)
the functions \( \psi^{(n)}_\epsilon \in \mathcal{V} \cap H^2(\mathbb{R}^3 \times \mathbb{R}^3) \) normalized in \( L^2(\mathbb{R}^3 \times \mathbb{R}^3) \),
\[ \psi^{(n)}_\epsilon := m^{(n)}_\epsilon \mathcal{T}_\epsilon \left( \phi^{(n)}_\epsilon \right) \] where \( \phi^{(n)}_\epsilon := \phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k \) and \( m^{(n)}_\epsilon = \left\| \mathcal{T}_\epsilon \left( \phi^{(n)}_\epsilon \right) \right\|^{-1}_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}, \) (73)
as well as the Rayleigh quotient
\[ \mu^{(n)}_\epsilon = \langle \psi^{(n)}_\epsilon, H_\epsilon \psi^{(n)}_\epsilon \rangle \] (74)
and the approximation
\[ \lambda^{(n)}_\epsilon = \lambda_0 - \sum_{k=0}^{n} C_n \epsilon^n \]
of \( \lambda_\epsilon \). When \( \epsilon \to 0 \), we have \( \mathcal{T}_\epsilon(\phi_0) \to 1 \) and therefore \( m^{(n)}_\epsilon \to 1 \). We know from [10, Section 2.4] that there exists a constant \( C \in \mathbb{R}_+ \) such that for \( \epsilon > 0 \) small enough
\[ \| \psi_\epsilon - \psi^{(3)}_\epsilon \|_{H^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C \epsilon^4, \quad |\lambda_\epsilon - \mu^{(3)}_\epsilon| \leq C \epsilon^8, \quad \text{and} \quad |\lambda_\epsilon - \lambda^{(6)}_\epsilon| \leq C \epsilon^7. \]
It follows from Theorem 5 that the \( \phi_n \)'s are in \( H^2(\mathbb{R}^3 \times \mathbb{R}^3) \). Since \( \mathcal{T}_\epsilon \) continuous on this space, we obtain that for all \( n \geq 3 \), there exists \( c_n \in \mathbb{R} \), such that for \( \epsilon > 0 \) small enough
\[ \| \psi_\epsilon - \psi^{(n)}_\epsilon \|_{H^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^4. \]
We infer from [10, Lemma 2.2 and Appendix A] that there exists a constant \( C \in \mathbb{R}_+ \) such that for all \( n \geq 3 \) there exists \( \epsilon > 0 \) such that for all \( 0 < \epsilon \leq \epsilon_n \),
\[ |\lambda_\epsilon - \mu^{(n)}_\epsilon| \leq C \| H_\epsilon \psi^{(n)}_\epsilon - \mu^{(n)}_\epsilon \psi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^2, \] (75)
\[ \| \psi_\epsilon - \psi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C \| H_\epsilon \psi^{(n)}_\epsilon - m^{(n)}_\epsilon \psi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \] (76)
(the first estimate above follows from the Kato-Temple inequality [16]). To proceed further, we need to evaluate the \( L^2 \)-norm of the residual \( r^{(n)}_\epsilon := H_\epsilon \psi^{(n)}_\epsilon - \mu^{(n)}_\epsilon \phi^{(n)}_\epsilon \). We have
\[ H_\epsilon \psi^{(n)}_\epsilon = m^{(n)}_\epsilon H_\epsilon \mathcal{T}_\epsilon(\phi^{(n)}_\epsilon) = m^{(n)}_\epsilon \mathcal{T}_\epsilon \left( (H_0 + V_\epsilon)(\phi^{(n)}_\epsilon) \right) = m^{(n)}_\epsilon \mathcal{T}_\epsilon \left( (H_0 + V_\epsilon)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) \right), \]
and thus,
\[ r^{(n)}_\epsilon = m^{(n)}_\epsilon \mathcal{T}_\epsilon \left( (H_0 + V_\epsilon)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) - (\lambda_0 - n \sum_{k=3}^{n} C_k \epsilon^k)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) + (\lambda^{(n)}_\epsilon - \mu^{(n)}_\epsilon)(\phi^{(n)}_\epsilon) \right) \]
\[ = m^{(n)}_\epsilon \mathcal{T}_\epsilon \left[ (H_0 + V_\epsilon)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) - (\lambda_0 - n \sum_{k=3}^{n} C_k \epsilon^k)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) \right. \]
\[ + (\lambda^{(n)}_\epsilon - \mu^{(n)}_\epsilon)(\phi^{(n)}_\epsilon) + \left. (V_\epsilon - \sum_{k=3}^{n} \epsilon^k \mathcal{B}(k))\phi^{(n)}_\epsilon \right]. \]
Using (9), we get
\[ (H_0 + \sum_{k=3}^{n} \epsilon^k \mathcal{B}(k))(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) - (\lambda_0 - \sum_{k=3}^{n} C_k \epsilon^k)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) \]
\[ = \epsilon^n \sum_{k=1}^{n} \epsilon^k \left( \sum_{j=k}^{n} \mathcal{B}^{(j)} \phi_{n+k-j} + \sum_{j=k}^{n} C_j \phi_{n+k-j} \right). \] (77)
Since $B^{(j)}$ are degree $(j-1)$ homogeneous functions (in cartesian coordinates) and the $\phi_n$’s decay exponentially in the sense of (28), there exists $K_n \in \mathbb{R}^+$ and $\epsilon_n > 0$ such that for all $0 < \epsilon \leq \epsilon_n$,

$$
\left\| \left( H_0 + \sum_{k=3}^{n} e^k B^{(k)} \right) (\phi_0 + \sum_{k=3}^{n} e^k \phi_k) - (\lambda_0 - \sum_{k=3}^{n} C_k e^k) (\phi_0 + \sum_{k=3}^{n} e^k \phi_k) \right\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq K_n \epsilon^{n+1}. \quad (78)
$$

It remains to bound $\| (V_0 - \sum_{k=3}^{n} e^k B^{(k)}) \psi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}$. From (6), (28) and (73), there exists $\epsilon_n > 0$, $\alpha_n > 0$ and $M_n \in \mathbb{R}^+$ such that for all $0 < \epsilon \leq \epsilon_n$

$$
\| e^{\alpha_n(|r_1| + |r_2|)} \phi^{(n)}_\epsilon \|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq M_n.
$$

Introducing

$$
\Omega_\epsilon = \{(r_1, r_2) \in \mathbb{R}^3 \times \mathbb{R}^3 : |r_1| + |r_2| < (2\epsilon)^{-1}\}.
$$

and the potentials defined by

$$
v^{(1)}_\epsilon (r_1, r_2) := |r_1 - \epsilon^{-1} e|^{-1}, \quad v^{(2)}_\epsilon (r_1, r_2) := |r_2 + \epsilon^{-1} e|^{-1}, \quad v^{(3)}_\epsilon (r_1, r_2) := |r_1 - r_2 - \epsilon^{-1} e|^{-1},
$$

we have,

$$
\| (V_0 - \sum_{k=3}^{n} e^k B^{(k)}) \phi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq \| (V_0 - \sum_{k=3}^{n} e^k B^{(k)}) \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} + \sum_{k=3}^{n} e^k \| B^{(k)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)}
$$

$$
+ \sum_{j=1}^{3} \| v^{(j)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} + \epsilon \| \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)}.
$$

We first see that

$$
\| \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} \leq e^{-\alpha_n (2\epsilon)^{-1}} \| e^{\alpha_n(|r_1| + |r_2|)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} \leq M_n e^{-\alpha_n (2\epsilon)^{-1}}.
$$

Next, as $B^{(k)}$ is a polynomial function, there exists a constant $B_n$ such as for all $0 < \epsilon \leq \epsilon_n$,

$$
\sum_{k=3}^{n} e^k \| B^{(k)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} \leq \sum_{k=3}^{n} e^k \| B^{(k)} e^{-\alpha_n(|r_1| + |r_2|)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)}
$$

$$
\leq M_n \sum_{k=3}^{n} e^k \| B^{(k)} e^{-\alpha_n(|r_1| + |r_2|)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} \leq B_n e^{3 \epsilon} e^{-\alpha_n (2\epsilon)^{-1}}.
$$

In addition, we have

$$
\sum_{j=1}^{3} \| v^{(j)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)} \leq \sum_{j=1}^{3} e^{-\alpha_n (2\epsilon)^{-1}} \| v^{(j)} \phi^{(n)}_\epsilon \|_{L^2(\Omega_\epsilon)}
$$

$$
\leq \sum_{j=1}^{3} e^{-\alpha_n (2\epsilon)^{-1}} \| v^{(j)} \phi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}
$$

$$
\leq 8 e^{-\alpha_n (2\epsilon)^{-1}} \| e^{\alpha_n(|r_1| + |r_2|)} \phi^{(n)}_\epsilon \|_{H^1(\mathbb{R}^3 \times \mathbb{R}^3)} \leq 8 e^{-\alpha_n (2\epsilon)^{-1}} M_n,
$$

where we have used the Hardy inequality in dimension 3

$$
\forall \phi \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \frac{|\phi(r)|^2}{|r|^2} \, dr \leq 4 \int_{\mathbb{R}^3} |\nabla \phi(r)|^2 \, dr
$$

to show that for any $\psi \in H^1(\mathbb{R}^3 \times \mathbb{R}^3)$,

$$
\| v^{(j)} \psi \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^2 = \int_{\mathbb{R}^3} \left( \int_{\mathbb{R}^3} \frac{|\psi(r_1, r_2)|^2}{|r_4 + (\epsilon^{-1} e_1)|^2} \, dr_4 \right) \, dr_3 \leq 4 \int_{\mathbb{R}^3} \left( \int_{\mathbb{R}^3} |\nabla r_3 \psi(r_1, r_2)|^2 \, dr_4 \right) \, dr_3 \leq 4 \| \nabla r_3 \psi \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)},
$$

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for \( j = 1, 2, \) and

\[
\|v^{(3)}_\epsilon\|_{L^2_\omega(\mathbb{R}^3 \times \mathbb{R}^3)}^2 \leq \frac{1}{8} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\psi(r_1, r_2)|^2}{|r_1 - r_2 - \epsilon^{-1} e|^2} \, dr_1 \, dr_2
\]

\[
\leq \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| (\nabla r_1 - \nabla r_2) \psi (r'_1 + r'_2, r'_1 - r'_2) \right|^2 \, dr'_1 \, dr'_2
\]

\[
= 4 \| (\nabla r_1 - \nabla r_2) \psi \|_{L^2_\omega(\mathbb{R}^3 \times \mathbb{R}^3)}^2 = 8 \| \nabla \psi \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^2.
\]

From the multipolar expansion of \( V_\epsilon \), we know that there exist \( c_n \in \mathbb{R}_+ \)

\[
\left| V_\epsilon (r_1, r_2) - \sum_{i=3}^{n} e^i B^{(i)}(r_1, r_2) \right| \leq c_n K^n \epsilon^{n+1}, \quad \text{whenever } |r_1| + |r_2| \leq K \leq (2\epsilon)^{-1}. \quad (81)
\]

Let us now show that (81) implies that there exists \( \bar{c}_n \in \mathbb{R}_+ \) such that for all \( 0 \leq K \leq (2\epsilon)^{-1} \),

\[
\sup_{|r_1| + |r_2| \leq K} \left| V_\epsilon (r_1, r_2) - \sum_{i=3}^{n} e^i B^{(i)}(r_1, r_2) \right| e^{-\alpha_n(|r_1| + |r_2|)} \leq \bar{c}_n \epsilon^{n+1}, \quad (82)
\]

This is immediate from (81) for \( K \leq 1 \), taking \( \bar{c}_n = c_n \). Now we let \( K > 1 \). Then (81) implies

\[
\sup_{(K/2) \leq (|r_1| + |r_2|) \leq K} \left| V_\epsilon (r_1, r_2) - \sum_{i=3}^{n} e^i B^{(i)}(r_1, r_2) \right| e^{-\alpha_n(|r_1| + |r_2|)} \leq c_n e^{-\alpha_n K^2 K^n \epsilon^{n+1}}.
\]

Applying this repeatedly for \( 2^{-j} K \) replacing \( K \) until \( 2^{-j} K < 1 \) yields (82), with

\[
\bar{c}_n = c_n \sup_{t \geq 0} e^{-\alpha_n t/2}.
\]

Applying (82) for \( K = (2\epsilon)^{-1} \) yields

\[
\|(V_\epsilon - \sum_{k=3}^{n} e^k B^{(k)})e^{-\alpha_n(|r_1| + |r_2|)}\|_{L^\infty(\Omega)} \leq \bar{c}_n \epsilon^{n+1},
\]

from which we obtain

\[
\|(V_\epsilon - \sum_{k=3}^{n} e^k B^{(k)})\phi^{(n)}_\epsilon\|_{L^2(\Omega)} \leq \|(V_\epsilon - \sum_{k=3}^{n} e^k B^{(k)})e^{-\alpha_n(|r_1| + |r_2|)}\|_{L^\infty(\Omega)} \|e^{\alpha_n(|r_1| + |r_2|)}\phi^{(n)}_\epsilon\|_{L^2(\Omega)}
\]

\[
\leq \bar{c}_n M_n \epsilon^{n+1}.
\]

Finally, we get

\[
\|(V_\epsilon - \sum_{k=3}^{n} e^k B^{(k)})\phi^{(n)}_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq \bar{c}_n M_n \epsilon^{n+1} + (8 + \epsilon + B_n \epsilon^3) M_n e^{-\alpha_n (2\epsilon)^{-1}}, \quad (83)
\]

Together with (78), this proves that there exists \( c_n' \in \mathbb{R}_+ \) such that for all \( 0 < \epsilon \leq \epsilon_n \),

\[
\|r^{(n)}_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = \|H_\epsilon \psi^{(n)}_\epsilon - \mu^{(n)}_\epsilon \psi^{(n)}_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n' \epsilon^{n+1}. \quad (84)
\]

It follows from (75)-(76) that for \( n \geq 3 \), there exists \( C \in \mathbb{R}_+ \) such that for all \( 0 < \epsilon \leq \epsilon_n \),

\[
|\lambda_\epsilon - \mu^{(n)}_\epsilon| \leq C \epsilon^{2(n+1)} \quad \text{and} \quad \|\psi_\epsilon - \psi^{(n)}_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C \epsilon^{n+1}. \quad (85)
\]

Then,

\[
\mu^{(n)}_\epsilon - \lambda^{(n)}_\epsilon = \langle \psi^{(n)}_\epsilon, H_\epsilon \psi^{(n)}_\epsilon - \lambda^{(n)}_\epsilon \psi^{(n)}_\epsilon \rangle
\]

\[
= m^{(n)}_\epsilon \left\langle \psi^{(n)}_\epsilon, T_\epsilon \left[ (V_\epsilon - \sum_{k=3}^{n} e^k B^{(k)})\phi^{(n)}_\epsilon + \epsilon \sum_{k=1}^{n} e^k \left( \sum_{j=k}^{n} B^{(j)} \phi_{n+j} + \sum_{j+k}^{n} C_j \phi_{n+k-j} \right) \right] \right\rangle.
\]
so that there exists a constant $c_n$ such that for $0 < \epsilon \leq \epsilon_n$,

$$
\left| \mu^{(n)}_\epsilon - \lambda^{(n)}_\epsilon \right| \leq 2 \left\| (V_\epsilon - \sum_{k=0}^{n} \epsilon^k E^{(k)}(n) \phi^{(n)}_\epsilon + \epsilon^n \sum_{k=1}^{n} \epsilon^k \left( \sum_{j=k}^{n} E^{(j)}(n) \phi_{n-k-j}^* \right)) \right\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^{n+1}.
$$

The error bounds on the eigenvalue errors in (12) follow from (85) and the above inequality.

Finally, the error $\xi^{(n)}_\epsilon = \psi_\epsilon - \psi^{(n)}_\epsilon$, as defined in [10], satisfies

$$
H_\epsilon \xi^{(n)}_\epsilon = \lambda_\epsilon \psi_\epsilon - H_\epsilon \psi^{(n)}_\epsilon = \lambda_\epsilon - \mu^{(n)}_\epsilon - r^{(n)}_\epsilon =: \eta^{(n)}_\epsilon.
$$

From (84)-(85), there exists a constant $c_n \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$,

$$
\| \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^{n+1} \quad \text{and} \quad \| \eta^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^{n+1}.
$$

In addition,

$$
-\frac{1}{2} \Delta \xi^{(n)}_\epsilon = - W_\epsilon \xi^{(n)}_\epsilon + \eta^{(n)}_\epsilon, \quad (86)
$$

where

$$
W_\epsilon(r_1, r_2) := - \frac{1}{|r_1 - (2\epsilon)^{-1}e|} - \frac{1}{|r_2 - (2\epsilon)^{-1}e|} - \frac{1}{|r_1 + (2\epsilon)^{-1}e|} - \frac{1}{|r_2 + (2\epsilon)^{-1}e|} + \frac{1}{|r_1 - r_2|} + \epsilon.
$$

Proceeding as in [10, Section 2.4], we use the Hardy inequality in $\mathbb{R}^3$ and the Cauchy-Schwarz inequality to obtain that

$$
\frac{1}{2} \| \nabla \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^2 = \langle \xi^{(n)}_\epsilon, - W_\epsilon \xi^{(n)}_\epsilon + \eta^{(n)}_\epsilon \rangle \\
\leq (10) \| \nabla \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} + \epsilon \| \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} + \| \eta^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \| \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)},
$$

$$
\frac{1}{2} \| \Delta \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^2 = \| - W_\epsilon \xi^{(n)}_\epsilon + \eta^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \\
\leq 10 \| \nabla \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} + \epsilon \| \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} + \| \eta^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}.
$$

It follows from (86) that there exists a constant $c_n \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$, $\| \Delta \xi^{(n)}_\epsilon \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^{n+1}$, and thus $\| \xi^{(n)}_\epsilon \|_{H^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq c_n \epsilon^{n+1}$.

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**A Appendix**

**A.1 Multipolar expansion of $V_\epsilon$**

We start from the well-known multipolar expansion of $\frac{1}{|r - Re|}$ in terms of Legendre polynomials

$$
\frac{1}{|r - Re|} = \frac{1}{R} \sum_{k=0}^{\infty} P_k \left( \frac{r \cdot e}{|r|} \right) \left( \frac{|r|}{R} \right)^k, \quad \text{for} \ |r| < R, \quad (87)
$$

which is a straightforward consequence of the definition of Legendre polynomials via their generating function [30]

$$
\forall -1 \leq x \leq 1, \quad (1 - 2xt + t^2)^{-1/2} = \sum_{k=0}^{\infty} P_k(x) t^k, \quad (88)
$$
Consequently, taking
\[-1 \leq x = \frac{r \cdot e}{|r|} \leq 1, \quad t = \frac{|r|}{R},\]

Since the Legendre polynomials are at most 1 in magnitude on the interval \([-1, 1]\), the sum in (88) converges absolutely for all \(|t| < 1\), and
\[
\left| \sum_{k=n}^{\infty} |P_k(x) t^k| \right| \leq \sum_{k=n}^{\infty} t^k = \frac{t^n}{1-t} \leq 2t^n, \quad \text{for all } |t| \leq \frac{1}{2}.
\]

Consequently,
\[
\left| \frac{1}{|r - R e|} - \frac{1}{R} \left( \sum_{k=0}^{n-1} P_k \left( \frac{r \cdot e}{|r|} \right) \left( \frac{|r|}{R} \right)^k \right) \right| \leq 2 \frac{|r|^n}{R^{n+1}}, \quad \text{for all } |r| \leq R/2. \tag{89}
\]

Recalling that \(P_0(x) = 1\), \(P_1(x) = x\) and
\[
V_{\epsilon}(r_1, r_2) = - \frac{1}{|r_1 - \epsilon^{-1} e|} - \frac{1}{|r_2 + \epsilon^{-1} e|} + \frac{1}{|r_1 - r_2 - \epsilon^{-1} e|} + \epsilon.
\]
with \(\epsilon = R^{-1}\), we deduce from (89) that
\[
\left| V_{\epsilon}(r_1, r_2) - \sum_{k=3}^{n} \epsilon^k B^{(k)}(r_1, r_2) \right| \leq 6K^n \epsilon^{n+1}, \quad \text{whenever } |r_1| + |r_2| \leq K \leq (2\epsilon)^{-1}, \tag{90}
\]
where the polynomial functions \(B^{(k)}\) are given by
\[
B^{(k)}(r_1, r_2) := P_{k-1} \left( \frac{r_1 - r_2 \cdot e}{|r_1 - r_2|} \right) |r_1 - r_2|^{k-1} - P_{k-1} \left( \frac{r_1 \cdot e}{|r_1|} \right) |r_1|^{k-1} - P_{k-1} \left( \frac{-r_2 \cdot e}{|r_2|} \right) |r_2|^{k-1}.
\]

This proves (81). To derive the expression (14) for the \(B^{(k)}\)’s, we first use the identities
\[
P_1(\sigma \cdot \sigma') = \left( \frac{4\pi}{2l + 1} \right) \sum_{m=-l}^{l} (-1)^m Y_{l}^m(\sigma) Y_{l}^m(\sigma'), \quad \sqrt{\frac{4\pi}{2l + 1}} Y_{l}^m(e) = \delta_{m,0},
\]
valid for all \(l \in \mathbb{N}, -l \leq m \leq l, \sigma, \sigma' \in S^2\) (recall that \(e\) is the unit vector of the z-axis), and get
\[
B^{(k)}(r_1, r_2) := \sqrt{\frac{4\pi}{2k - 1}} Y_{k-1}^0 \left( \frac{r_1 - r_2}{|r_1 - r_2|} \right) |r_1 - r_2|^{k-1} - Y_{k-1}^0 \left( \frac{r_1}{|r_1|} \right) |r_1|^{k-1} - Y_{k-1}^0 \left( \frac{-r_2}{|r_2|} \right) |r_2|^{k-1}.
\]

We next use the addition formula [28] stating that for \(l \in \mathbb{N}, r_1, r_2 \in \mathbb{R}^3\),
\[
\sqrt{\frac{4\pi}{2l + 1}} Y_{l}^0 \left( \frac{r_1 - r_2}{|r_1 - r_2|} \right) |r_1 - r_2|^{l} = \sum_{l_1 + l_2 = l} \sum_{m=-\min(l_1, l_2)}^{\min(l_1, l_2)} G_{c}(l_1, l_2, m) r_1^{l_1} Y_{l_1}^m \left( \frac{r_1}{|r_1|} \right) r_2^{l_2} Y_{l_2}^{-m} \left( \frac{r_2}{|r_2|} \right),
\]
where
\[
G_{c}(l_1, l_2, m) = (-1)^{l_2} \frac{4\pi}{((2l_1 + 1)(2l_2 + 1))^{1/2}} \left( \frac{l_1 + l_2}{l_1 + m} \right)^{1/2} \left( \frac{l_1 + l_2}{l_1 - m} \right)^{1/2},
\]
\[
= (-1)^{l_2} \frac{4\pi(l_1 + l_2)!}{((2l_1 + 1)(2l_2 + 1)(l_1 + m)!(l_2 + m)!(l_1 - m)!(l_2 - m)!)^{1/2}}.
\]
As for \(G_{c}(l, 0, 0) = G_{c}(0, l, 0) = \frac{4\pi}{(2l + 1)^{3/2}}\) and \(Y_{0}^0 = \frac{1}{\sqrt{4\pi}}\), we finally obtain (14).
B  Wigner \((2n + 1)\) rule

Using the notation in (73), we consider the Rayleigh quotients

\[
\mu_\epsilon^{(n)} = \langle \psi_\epsilon^{(n)}, H_\epsilon \psi_\epsilon^{(n)} \rangle \quad \text{and} \quad \bar{\mu}_\epsilon^{(n)} = \frac{\langle \phi_\epsilon^{(n)}, \left( H_0 + \sum_{i=3}^{2n+1} \epsilon^i B^{(i)} \right) \phi_\epsilon^{(n)} \rangle}{\| \phi_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}}
\]

(recall that \(\| \psi_\epsilon^{(n)} \|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1\)). Let

\[
\eta_\epsilon^{(n)} := (H_0 + V_\epsilon) \phi_\epsilon^{(n)}, \quad \nu_\epsilon^{(n)} := (V_\epsilon - \sum_{i=3}^{2n+1} \epsilon^i B^{(i)}) \phi_\epsilon^{(n)} \quad \text{and} \quad \xi_\epsilon^{(n)} := (T^*_\epsilon T_\epsilon - 1) \phi_\epsilon^{(n)}.
\]

We deduce from the boundedness of the \(\phi_k\)'s in \(H^2(\mathbb{R}^3 \times \mathbb{R}^3)\), the Hardy inequality in \(\mathbb{R}^3\), and the estimates (28) and (81), that there exist \(C \in \mathbb{R}_+, \beta_n > 0\) and \(\epsilon_n > 0\) such that for all \(0 \leq \epsilon \leq \epsilon_n\)

\[
\| \phi_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq 2, \quad \| \eta_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C, \quad \| \eta_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C\epsilon^{2n+2}, \quad \| \xi_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} \leq C\epsilon^{-\beta_n \epsilon},
\]

proceeding as in the proof of (83) to establish the third inequality. It follows from (12) and the above bounds that

\[
\bar{\mu}_\epsilon^{(n)} = \lambda_\epsilon + \bar{\mu}_\epsilon^{(n)} - \mu_\epsilon^{(n)} + O(\epsilon^{2n+2})
\]

\[
= \lambda_\epsilon + \frac{\langle \phi_\epsilon^{(n)}, (H_0 + \sum_{i=3}^{2n+1} \epsilon^i B^{(i)}) \phi_\epsilon^{(n)} \rangle}{\| \phi_\epsilon^{(n)} \|^2_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}} + \frac{\langle T^*_\epsilon T_\epsilon \phi_\epsilon^{(n)}, (H_0 + V_\epsilon) \phi_\epsilon^{(n)} \rangle}{\langle T^*_\epsilon T_\epsilon \phi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \rangle} + O(\epsilon^{2n+2})
\]

\[
= \lambda_\epsilon - \frac{\langle \phi_\epsilon^{(n)}, \nu_\epsilon^{(n)} \rangle}{\langle \phi_\epsilon^{(n)}, \nu_\epsilon^{(n)} \rangle} \cdot \frac{\langle \xi_\epsilon^{(n)}, \eta_\epsilon^{(n)} \rangle - \langle \xi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \rangle \langle \phi_\epsilon^{(n)}, \eta_\epsilon^{(n)} \rangle}{\langle \phi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \rangle} + O(\epsilon^{2n+2})
\]

\[
= \lambda_\epsilon + O(\epsilon^{2n+2}) = -1 - \sum_{k=6}^{2n+1} C_k \epsilon^k + O(\epsilon^{2n+2}).
\]

Thus, the coefficients \(C_k\) for \(k \leq 2n + 1\) can be computed from the Taylor expansion of \(\bar{\mu}_\epsilon^{(n)}\) up to order \((2n + 1)\), which only involves the \(\phi_k\)'s for \(k \leq n\), and the \(B^{(k)}\)'s for \(k \leq (2n + 1)\). To obtain a computable expression of the coefficients \(C_{2n}\) and \(C_{2n+1}\), we first use Equation (9), which can be rewritten as

\[
H_0 \phi_k + \sum_{j=3}^{k} B^{(j)} \phi_{k-j} = -C_0 \phi_k - \sum_{j=0}^{k} C_j \phi_{k-j} = -\sum_{j=0}^{k} C_j \phi_{k-j}, \quad (91)
\]

with \(C_0 = 1\) and \(C_i = 0\) for \(i = 1, \ldots, 5\), to get that for all \(n \geq 1\)

\[
\nu_\epsilon^{(n)} = \langle \phi_\epsilon^{(n)}, \left( H_0 + \sum_{i=3}^{2n+1} \epsilon^i B^{(i)} \right) \phi_\epsilon^{(n)} \rangle
\]

\[
= -\sum_{l=0}^{n} \epsilon^l \sum_{i=0}^{l} \left( \langle \phi_\epsilon^{(n)}, \sum_{j=0}^{l-i} C_j \phi_{l-i-j} \rangle + \epsilon^n \sum_{l=i}^{n-l-i} \left( -\sum_{j=0}^{l-i} C_j \phi_{n+l-i-j} \right) + \sum_{j=0}^{n-i} \langle \phi_\epsilon^{(n)}, \sum_{j=0}^{n-l-i-j} B^{(n+l-i-j)} \phi_j \rangle \right)
\]

\[
+ \epsilon^{2n+1} \sum_{i=0}^{n} \langle \phi_\epsilon^{(n)}, \sum_{j=0}^{n} B^{(2n+1-i-j)} \phi_j \rangle + O(\epsilon^{2n+2}). \quad (92)
\]

In addition, we have

\[
\| \phi_\epsilon^{(n)} \|^2 = \langle \sum_{i=0}^{n} \epsilon^i \phi_i, \sum_{i=0}^{n} \epsilon^i \phi_j \rangle = 1 + \sum_{k=1}^{n} \epsilon^k \sum_{i=0}^{k} \langle \phi_i, \phi_{n+k-i} \rangle + \epsilon^n \sum_{k=1}^{n} \epsilon^k \sum_{i=k}^{n} \langle \phi_i, \phi_{n+k-i} \rangle,
\]

and, using the relation \(\sum_{k=0}^{n-k} \langle \phi_i, \phi_{k-i} \rangle = 0\) derived from (10), we get

\[
\| \phi_\epsilon^{(n)} \|^2 = 1 + \epsilon^n \sum_{k=1}^{n} \epsilon^k \sum_{i=k}^{n} \langle \phi_i, \phi_{n+k-i} \rangle. \quad (93)
\]
Il follows from (92)-(93) that
\[ \bar{\mu}_e^{(n)} = \frac{\mu_e^{(n)}}{\|\phi_e^{(n)}\|^2} = -\sum_{k=0}^{2n+1} C_k \epsilon^k + O(\epsilon^{2n+2}), \]
with
\[ C_{2n} = \left\langle \phi_n, \sum_{j=0}^{n} C_j \phi_{n-j} \right\rangle - \sum_{i=0}^{n-1} \left\langle \phi_i, \sum_{j=0}^{n} B^{(2n-i-j)} \phi_j \right\rangle - \sum_{k=1}^{n} \sum_{i=0}^{n} \left\langle \phi_i, \phi_{n+k-i} \right\rangle \sum_{i=0}^{n-k} \left\langle \phi_i, \sum_{j=0}^{n-k-i} C_j \phi_{n-k-i-j} \right\rangle, \]
and
\[ C_{2n+1} = -\sum_{i=0}^{n} \left\langle \phi_i, \sum_{j=0}^{n} B^{(2n+1-i-j)} \phi_j \right\rangle - \sum_{k=1}^{n} \sum_{i=0}^{n} \left\langle \phi_i, \phi_{n+k-i} \right\rangle \sum_{i=0}^{n-k} \left\langle \phi_i, \sum_{j=0}^{n-k-i} C_j \phi_{n+1-k-i-j} \right\rangle. \]

C Computation of the integrals \( S_n \) in (57)

Recall that
\[ S_n = \int_0^{+\infty} r^3 e^{-r} \varphi_{n,1}(r) dr, \]
where
\[ \varphi_{n,1} = \sqrt{\left( \frac{2}{n} \right)^3 \frac{(n-2)!}{2n(n+1)!}} \left( \frac{2r}{n} \right) L_n^{(3)} \left( \frac{2r}{n} \right) e^{-r/n}, \]
where the associated Laguerre polynomials of the second kind \( L_n^{(m)} \), \( n, m \in \mathbb{N} \), satisfy the following properties [1, Section 22.2]:

- for all \( k, k', m, n \in \mathbb{N} \),
  \[ \int_0^{+\infty} x^m L_k^{(m)}(x) L_{k'}^{(m)}(x) e^{-x} dx = \frac{(k+m)!}{k!} \delta_{k,k'}; \]
- for all \( \gamma \in \mathbb{C} \) such that \( \Re(\gamma) > -\frac{1}{2} \), and \( m \in \mathbb{N} \),
  \[ e^{-\gamma x} = \sum_{k=0}^{+\infty} \frac{\gamma^k}{(1+\gamma)^{k+m+1}} L_k^{(m)}(x); \]
- for all \( k, m \in \mathbb{N} \),
  \[ x L_k^{(m+1)}(x) = (k+m+1) L_k^{(m)}(x) - (k+1) L_{k+1}^{(m)}(x). \]

By a change of variable, we obtain
\[ S_n = \frac{n^2}{8} \sqrt{(n-2)!} \int_n I_n \text{ with } I_n := \int_0^{+\infty} x^4 L_n^{(3)}(x) e^{-r/n} dx. \]

Applying (95) for \( \gamma = \frac{n-1}{2} \), and \( m = 4 \), then (96) for \( m = 3 \), and finally (94) for \( m = 3 \), we obtain
\[ I_n = \int_0^{+\infty} x^4 L_{n-2}^{(3)} \left( \sum_{k=0}^{+\infty} \frac{2^k(n-1)^k}{(n+1)k+5} L_k^{(4)}(x) \right) e^{-x} dx \]
\[ = \int_0^{+\infty} x^3 L_{n-2}^{(3)} \left( \sum_{k=0}^{+\infty} \frac{2^k(n-1)^k}{(n+1)k+5} \left( (k+4) L_k^{(3)}(x) - (k+1) L_{k+1}^{(3)}(x) \right) \right) e^{-x} dx \]
\[ = \sum_{k=0}^{+\infty} \frac{2^k(n-1)^k}{(n+1)k+5} \left( (k+4) \frac{(k+3)!}{k!} \delta_{k,n-2} - (k+1) \frac{(k+4)!}{(k+1)!} \delta_{k+1,n-2} \right) \]
\[ = \frac{2^3(n-1)^{n-2}}{(n+1)^{n+3}} (n+2) \frac{(n+1)!}{(n-2)!} - \frac{2^5(n-1)^{n-3}}{(n+1)^{n+2}} (n-2) \frac{(n+1)!}{(n-2)!} \]
\[ = \frac{2^6(n-1)^{n-3}}{(n+1)^{n+3}} (n+1)! \]
\[ \frac{(n-2)!}{(n-2)!}. \]
Finally, we get

\[ S_n = 8n^3 \frac{(n-1)^{n-3}}{(n+1)^{n+3}} \sqrt{\frac{(n+1)!}{(n-2)!}}. \]

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