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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., 50:381–410, 2018] 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.

Keywords. Electronic structure; Van der Waals force; hydrogen molecule.

AMS subject classifications. 35Q40; 81Q05; 81Q15.

1. Introduction

Van der Waals interactions, first introduced in 1873 to reproduce experimental results on simple gases [37], have proved to also play an essential role in complex systems in the condensed phase, such as biological molecules [9, 32] and 2D materials [19]. The many-body quantum mechanical nature of the dispersive van der Waals interaction has been elucidated by London in the 1930s [25]. Since then, the development of reduced models and numerical methods to compute approximations of interatomic and intermolecular interactions has given rise to a very large number of contributions in the physical chemistry literature (see e.g. the recent review [40] and references therein).

The first mathematical result on long-range interactions between quantum systems is due to Morgan and Simon [27]. Inspired by the works of Ahlrichs in [2], they proved that the interaction energy between two neutral or charged atoms (in the Born-Oppenheimer approximation with spinless electrons in their ground state) admits an asymptotic expansion in the inverse atomic distance R^{-1}. They also study in more detail the special case of the H_2^+ ion (see also the contributions [11, 16, 17, 20] in the physics literature). They show that the asymptotic series is Borel summable and compute numerically the first 38 coefficients; based on these numerical results, they conclude that the series probably diverges. A few years later, Lieb and Thiring [24] proved a universal lower bound of the interaction energy between molecular clusters in the large separation regime; this bound involves pair-wise interactions of the form $R_{i,j}^{-6}$, where $R_{i,j}$ is the distance between clusters i and j. It was established only recently by Anapolitanos and Sigal that for neutral atoms (and under assumptions on ionization energies and electron affinities satisfied for all chemical elements for which experimental data are available), the leading term of the interaction energy is asymptotically of the from $\sum_{1\le i<j\le M} \sigma_{i,j} R_{i,j}^{-6}$ when the $R_{i,j}$'s go to infinity, where the coefficients $\sigma_{i,j}$ only depend on the atomic number of atoms i and j (see also [4, 8]). Recent articles have studied higher-order terms up to $1/R^9$ [10], molecules [5, 6] and forces, i.e. the derivatives of

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the interaction energy with respect to atomic positions [7]. The relativistic framework was considered in [23].

In a recent paper [13], 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 [29] and [15] 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 [28]. 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 [28] 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 [3, 14, 35] 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 [26] are needed. The third order [41] is sufficient for C_{11}, C_{13} and C_{15}. Moreover, the polarizabilities method can be derived also for atoms other than hydrogen as well as for three-body interaction [14]. A comparison of the numerical results is explored in Section 3.1.

One can also compute the expansion coefficients using basis states as in [18]. 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 [34] 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 [13] and gave a value of C_6 agreeing with [28]. 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 [34], 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 [33, Section 7.3] to compute coefficients up to C_{19}, given that C_6 has been computed in [13]. 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.

The method presented in this article is specific to the hydrogen molecule H_2. It could be applied to the helium hydride ion HeH^+ as well, but is restricted to two-electron diatomic systems. A track to go beyond would be to try and reformulate in terms of lower-dimensional PDEs the approach introduced in [30] to compute the high-order dispersion coefficients for the interaction of helium atoms. This is left to future work.

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), $e = 1$ (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 4.36×10^{-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 $\mathbf{r}_1$ and $\mathbf{r}_2$ 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 $\mathbf{e}$ 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 ϵ of the ground state energy and wave function. Note that in [13], 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 [21], its wave function can be written as

$$\psi_\epsilon(\mathbf{r}_1, \mathbf{r}_2) \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}, \tag{2.1}$$

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

$$H_\epsilon \psi_\epsilon = \lambda_\epsilon \psi_\epsilon, \quad \|\psi_\epsilon\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)} = 1, \tag{2.2}$$

where for $\epsilon > 0$, the Hamiltonian H_ϵ 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

$$\begin{aligned} H_\epsilon = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} &- \frac{1}{|\mathbf{r}_1 - (2\epsilon)^{-1}\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 - (2\epsilon)^{-1}\mathbf{e}|} \\ &- \frac{1}{|\mathbf{r}_1 + (2\epsilon)^{-1}\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + (2\epsilon)^{-1}\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \epsilon, \end{aligned}$$

where $\Delta_{\mathbf{r}_k}$ is the Laplace operator with respect to the variables $\mathbf{r}_k \in \mathbb{R}^3$. The first two terms of H_ϵ 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_ϵ is symmetric ($\psi_\epsilon(\mathbf{r}_1, \mathbf{r}_2) = \psi_\epsilon(\mathbf{r}_2, \mathbf{r}_1)$) so that the wave function defined by (2.1) does satisfy the Pauli principle (the anti-symmetry is entirely carried by the spin component). It is well-known [4, 8, 13, 27] that

$$\lambda_\epsilon = -1 - C_6\epsilon^6 + o\left(\epsilon^6\right).$$

The computation of λ_ϵ (and ψ_ϵ) 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

$$\tau_\epsilon f(\mathbf{r}_1,\mathbf{r}_2) = f(\mathbf{r}_1 + (2\epsilon)^{-1}\mathbf{e}, \mathbf{r}_2 - (2\epsilon)^{-1}\mathbf{e}) = f(\mathbf{r}_1 + \tfrac{1}{2}R\mathbf{e}, \mathbf{r}_2 - \tfrac{1}{2}R\mathbf{e}), \quad R = \epsilon^{-1},$$

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

$$\mathcal{C}\phi(\mathbf{r}_1,\mathbf{r}_2) = \phi(\mathbf{r}_2,\mathbf{r}_1), \qquad \mathcal{S} = \frac{1}{\sqrt{2}}(\mathcal{I}+\mathcal{C}),$$

where $\mathcal{I}$ denotes the identity operator, as well as the "asymptotically unitary" operator

$$\mathcal{T}_\epsilon = \mathcal{S}\tau_\epsilon. \tag{2.3}$$

It is shown in [13] that

$$H_\epsilon \mathcal{T}_\epsilon = \mathcal{T}_\epsilon\big(H_0 + V_\epsilon\big), \tag{2.4}$$

where H_0 is the reference non-interacting Hamiltonian

$$H_0 = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{|\mathbf{r}_1|} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_2|},$$

and V_ϵ the correlation potential

$$V_\epsilon(\mathbf{r}_1,\mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 - \epsilon^{-1}\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \epsilon^{-1}\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \epsilon^{-1}\mathbf{e}|} + \epsilon. \tag{2.5}$$

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

$$\big\langle \mathcal{T}_\epsilon f, \mathcal{T}_\epsilon g\big\rangle = \big\langle f, g\big\rangle + \big\langle \mathcal{C}f, \tau_{\epsilon/2} g\big\rangle \underset{\epsilon\to 0}{\longrightarrow} \big\langle f, g\big\rangle.$$

It follows from (2.4) that if (λ,ϕ) is a normalized eigenstate of $H_0 + V_\epsilon$, that is (λ,ϕ) 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 [13, 42] that both H_ϵ 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 $\mathbb{R}^{3\times 3}$. Since $\mathcal{T}_\epsilon$ preserves positivity, we infer that H_ϵ and $H_0 + V_\epsilon$ share the same ground state eigenvalue λ_ϵ and that if ϕ_ϵ 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_ϵ.

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

$$\lambda_0 = -1, \qquad \phi_0(\mathbf{r}_1,\mathbf{r}_2) = \pi^{-1} e^{-(|\mathbf{r}_1|+|\mathbf{r}_2|)}, \tag{2.6}$$

of H_0. Using a multipolar expansion, we have

$$V_\epsilon(\mathbf{r}_1,\mathbf{r}_2)=\sum_{n=3}^{+\infty}\epsilon^n\mathcal{B}^{(n)}(\mathbf{r}_1,\mathbf{r}_2), \tag{2.7}$$

where homogeneous polynomial functions $\mathcal{B}^{(n)}$, $n\geq 3$ are specified below (see Equation (2.14)), the convergence of the series being uniform on every compact subset of $\mathbb{R}^3\times\mathbb{R}^3$. Assuming that λ_ϵ and ϕ_ϵ can be Taylor expanded as

$$\lambda_\epsilon=\lambda_0-\sum_{n=1}^{+\infty}C_n\epsilon^n \quad \text{and} \quad \phi_\epsilon=\sum_{n=0}^{+\infty}\epsilon^n\phi_n, \qquad \text{(formal expansions)} \tag{2.8}$$

(we use the standard historical notation $-C_n$ instead of λ_n for the coefficients of the eigenvalue λ_ϵ) inserting these expansions in the equations $(H_0+V_\epsilon)\phi_\epsilon=\lambda_\epsilon\phi_\epsilon$, $\|\phi_\epsilon\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}=1$, and identifying the terms of order n in ϵ, 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 2.1. *The triangular system*

$$\forall n\geq 1, \qquad (H_0-\lambda_0)\phi_n=-\sum_{k=3}^{n}\mathcal{B}^{(k)}\phi_{n-k}-\sum_{k=1}^{n}C_k\phi_{n-k}, \tag{2.9}$$

$$\langle\phi_0,\phi_n\rangle=-\frac{1}{2}\sum_{k=1}^{n-1}\langle\phi_k,\phi_{n-k}\rangle, \tag{2.10}$$

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 $(\mathbb{R}\times H^2(\mathbb{R}^3\times\mathbb{R}^3))^{\mathbb{N}^*}$. 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 ϕ_n are real-valued.

Note that $(C_1,\phi_1)=(C_2,\phi_2)=0$ directly follows from the fact that the first nonvanishing term in the expansion (2.7) of V_ϵ is $\epsilon^3\mathcal{B}^{(3)}$. The formal expansions (2.8) are in fact asymptotic expansions as established in the following theorem, whose proof is provided in Section 4.2. Note that an inequality of the form (2.12) was established in a more general framework in [27, Theorem 3.5].

Theorem 2.1. *Let $\psi_\epsilon\in H^2(\mathbb{R}^3\times\mathbb{R}^3)$ be the positive $L^2(\mathbb{R}^3\times\mathbb{R}^3)$-normalized ground state of H_ϵ and λ_ϵ the associated ground-state energy:*

$$H_\epsilon\psi_\epsilon=\lambda_\epsilon\psi_\epsilon, \quad \|\psi_\epsilon\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}=1, \quad \psi_\epsilon>0 \text{ a.e. on } \mathbb{R}^3\times\mathbb{R}^3. \tag{2.11}$$

Let (ϕ_0,λ_0) be as in (2.6), $((C_n,\phi_n))_{n\in\mathbb{N}^*}$ the unique solution of (2.9) in $(\mathbb{R}\times H^2(\mathbb{R}^3\times\mathbb{R}^3))_{n\in\mathbb{N}^*}$, and $\mathcal{T}_\epsilon$ the "almost unitary" symmetrization operator defined in (2.3). Then, for all $n\in\mathbb{N}$, there exists $\epsilon_n>0$ and $K_n\in\mathbb{R}_+$ such that for all $0<\epsilon\leq\epsilon_n$,

$$\left\|\psi_\epsilon-\psi_\epsilon^{(n)}\right\|_{H^2(\mathbb{R}^3\times\mathbb{R}^3)}\leq K_n\epsilon^{n+1}, \quad \left|\lambda_\epsilon-\lambda_\epsilon^{(n)}\right|\leq K_n\epsilon^{n+1}, \quad \left|\lambda_\epsilon-\mu_\epsilon^{(n)}\right|\leq K_n\epsilon^{2(n+1)}, \tag{2.12}$$

where

$$\psi_\epsilon^{(n)}:=\frac{\mathcal{T}_\epsilon\left(\phi_0+\sum_{k=3}^{n}\epsilon^k\phi_k\right)}{\|\mathcal{T}_\epsilon\left(\phi_0+\sum_{k=3}^{n}\epsilon^k\phi_k\right)\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}}, \; \lambda_\epsilon^{(n)}:=\lambda_0-\sum_{k=6}^{n}C_k\epsilon^k, \; \mu_\epsilon^{(n)}=\langle\psi_\epsilon^{(n)}|H_\epsilon|\psi_\epsilon^{(n)}\rangle.$$

Let us point out that in view of the last two bounds in (2.12), the series expansion of $\mu_\epsilon^{(n)}$ in ϵ up to order $(2n+1)$, which can be computed from the ϕ_k's for $0 \le k \le n$, is given by

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

Therefore, the knowledge of the ϕ_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 2.1 (van der Waals forces). It follows from the Hellmann-Feynman theorem that the van der Waals force $\mathbf{F}_\epsilon$ acting on the nucleus located at $(2\epsilon)^{-1}\mathbf{e}$ is given by

$$\mathbf{F}_\epsilon = \int_{\mathbb{R}^3} \frac{(\mathbf{r} - (2\epsilon)^{-1}\mathbf{e})}{|\mathbf{r} - (2\epsilon)^{-1}\mathbf{e}|^3} \rho_\epsilon(\mathbf{r})\, d\mathbf{r} \text{ with } \rho_\epsilon(\mathbf{r}) = 2\int_{\mathbb{R}^3} |\psi_\epsilon(\mathbf{r},\mathbf{r}')|^2\, d\mathbf{r}' \text{ (electronic density).}$$

Introducing the approximation $\mathbf{F}_\epsilon^{(n)}$ of $\mathbf{F}_\epsilon$ computed from $\psi_\epsilon^{(n)}$ as

$$\mathbf{F}_\epsilon^{(n)} = \int_{\mathbb{R}^3} \frac{(\mathbf{r} - (2\epsilon)^{-1}\mathbf{e})}{|\mathbf{r} - (2\epsilon)^{-1}\mathbf{e}|^3} \rho_\epsilon^{(n)}(\mathbf{r})\, d\mathbf{r} \quad \text{with} \quad \rho_\epsilon^{(n)}(\mathbf{r}) = 2\int_{\mathbb{R}^3} |\psi_\epsilon^{(n)}(\mathbf{r},\mathbf{r}')|^2\, d\mathbf{r}',$$

we obtain from the Cauchy-Schwarz inequality, the Hardy inequality in $\mathbb{R}^3$, and (2.12) that

$$|\mathbf{F}_\epsilon - \mathbf{F}_\epsilon^{(n)}| \le 8\|\psi_\epsilon - \psi_\epsilon^{(n)}\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} \|\psi_\epsilon + \psi_\epsilon^{(n)}\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} \le K_n' \epsilon^{n+1}$$

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

$$\mathbf{F}_\epsilon = -\left(\sum_{k=6}^{n} n C_n \epsilon^{n+1}\right) \mathbf{e} + O(\epsilon^{n+1}).$$

This extends the result $\mathbf{F}_\epsilon = -6C_6\epsilon^7\mathbf{e} + O(\epsilon^8)$ proved in [7, 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 $\mathcal{B}^{(n)}$ 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 $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ of $\mathbb{R}^3$ for which $\mathbf{e}_3 = \mathbf{e}$, so that

$$\begin{aligned} \mathbf{r}_i &= r_i\big(\sin(\theta_i)\cos(\phi_i)\mathbf{e}_1 + \sin(\theta_i)\sin(\phi_i)\mathbf{e}_2 + \cos(\theta_i)\mathbf{e}\big), \\ &\cos(\theta_i) = \mathbf{r}_i \cdot \mathbf{e}, \quad \text{and} \quad r_i = |\mathbf{r}_i|, \quad i = 1,2, \end{aligned} \tag{2.13}$$

it holds that for all $n \ge 3$,

$$\mathcal{B}^{(n)}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{(l_1,l_2)\in B_n} r_1^{l_1} r_2^{l_2} \sum_{-\min(l_1,l_2)\le m\le \min(l_1,l_2)} G_{\mathrm{c}}(l_1,l_2,m) Y_{l_1}^m(\theta_1,\phi_1) Y_{l_2}^{-m}(\theta_2,\phi_2), \tag{2.14}$$

$$= \sum_{(l_1,l_2)\in B_n} r_1^{l_1} r_2^{l_2} \sum_{-\min(l_1,l_2)\le m\le \min(l_1,l_2)} G_{\mathrm{r}}(l_1,l_2,m) \mathcal{Y}_{l_1}^m(\theta_1,\phi_1) \mathcal{Y}_{l_2}^m(\theta_2,\phi_2), \tag{2.15}$$

where $(Y_l^m)_{l\in\mathbb{N},\, m=-l,-l+1,\cdots,l-1,l}$ and $(\mathcal{Y}_l^m)_{l\in\mathbb{N},\, m=-l,-l+1,\cdots,l-1,l}$ are respectively the complex and real spherical harmonics , and where

$$B_n = \{(l_1,l_2) \,:\, l_1+l_2 = n-1,\ l_1,l_2 \neq 0\} = \{(l, n-1-l) \,:\, 1 \le l \le n-2\}. \quad (2.16)$$

The coefficients $G_{\rm c}(l_1,l_2,m)$ and $G_{\rm r}(l_1,l_2,m)$ are respectively given by

$$G_{\rm c}(l_1,l_2,m) := (-1)^{l_2} \frac{4\pi(l_1+l_2)!}{\big((2l_1+1)(2l_2+1)(l_1-m)!(l_1+m)!(l_2-m)!(l_2+m)!\big)^{1/2}}, \quad (2.17)$$
$$G_{\rm r}(l_1,l_2,m) := (-1)^m G_{\rm c}(l_1,l_2,m).$$

Both expansions (2.14) and (2.15) are useful: (2.14) will be used in the proof of Theorem 2.2 to establish formula (2.26), which has a simpler and more compact form in the complex spherical harmonics basis. On the other hand, (2.15) allows one to work with real-valued functions.

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

$$\Omega = \mathbb{R}_+^* \times \mathbb{R}_+^*,$$

extending the technique of Slater and Kirkwood for C_6 [34], modified in [13]. For each angular momentum quantum number $l \in \mathbb{N}$, we denote by

$$\kappa_l(r) = \frac{l(l+1)}{2r^2} - \frac{1}{r} - \frac{1}{2}\lambda_0 = \frac{l(l+1)}{2r^2} - \frac{1}{r} + \frac{1}{2}, \quad (2.18)$$

and we consider the boundary value problem: given $f \in L^2(\Omega)$

$$\begin{cases} \text{find } T \in H_0^1(\Omega) \text{ such that} \\ -\dfrac{1}{2}\Delta T(r_1,r_2) + (\kappa_{l_1}(r_1) + \kappa_{l_2}(r_2))\, T = f(r_1,r_2) \quad \text{in } \mathcal{D}'(\Omega). \end{cases} \quad (2.19)$$

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 (2.19) is well posed in $H_0^1(\Omega)$. For $l_1 = l_2 = 0$, this problem is well-posed in

$$\widetilde{H_0^1}(\Omega) = \left\{ v \in H_0^1(\Omega) \,:\, \int_\Omega v(r_1,r_2) e^{-r_1-r_2}\, r_1 r_2 \,{\rm d}r_1 {\rm d}r_2 = 0 \right\},$$

provided that the compatibility condition

$$\int_\Omega f(r_1,r_2) e^{-r_1-r_2}\, r_1 r_2 \,{\rm d}r_1 {\rm d}r_2 = 0 \quad (2.20)$$

is fulfilled. Problem (2.19) is useful to solve the Rayleigh–Schrödinger system (2.9)-(2.10) thanks to the following lemma, proved in Section 4.1. We denote by

$$\phi_0^\perp := \left\{ \psi \in L^2(\mathbb{R}^3 \times \mathbb{R}^3) \,:\, \langle \phi_0, \psi \rangle = 0 \right\}.$$

Note that the condition (2.20) is equivalent to $\langle \phi_0, \frac{f(r_1,r_2)}{r_1 r_2} \rangle = 0$.

Lemma 2.2. *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 $\psi \in H^2(\mathbb{R}^3 \times \mathbb{R}^3) \cap \phi_0^\perp$ solution to the equation*

$$(H_0 - \lambda_0)\psi = F \quad \textit{with} \quad F := \frac{f(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2). \tag{2.21}$$

(1) *If $(l_1, l_2) \neq (0, 0)$, then the unique solution to (2.21) in $H^2(\mathbb{R}^3 \times \mathbb{R}^3)$ is*

$$\psi = \frac{T(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2), \tag{2.22}$$

where T is the unique solution to (2.19) in $H_0^1(\Omega)$;

(2) *If $(l_1, l_2) = (0, 0)$, and if the compatibility condition (2.20) is satisfied, then the unique solution to (2.21) in $H^2(\mathbb{R}^3 \times \mathbb{R}^3) \cap \phi_0^\perp$ is*

$$\psi = \frac{1}{4\pi} \frac{T(r_1, r_2)}{r_1 r_2},$$

where T is the unique solution to (2.19) in $\widetilde{H}_0^1(\Omega)$.

In addition, if f decays exponentially at infinity, then so does T, hence ψ, 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 $f \in L^2(\Omega)$

$$\|e^{\alpha(r_1+r_2)} T\|_{H^1(\Omega)} \leq C_\alpha \|e^{\eta(r_1+r_2)} f\|_{L^2(\Omega)}, \tag{2.23}$$

$$\|e^{\alpha(|\mathbf{r}_1|+|\mathbf{r}_2|)} \psi\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq C_\alpha \|e^{\eta(|\mathbf{r}_1|+|\mathbf{r}_2|)} F\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}, \tag{2.24}$$

$$\|e^{\alpha(|\mathbf{r}_1|+|\mathbf{r}_2|)} \psi\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} \leq C_\alpha (1 + 4l_1(l_1+1) + 4l_2(l_2+1))^{1/2} \|e^{\eta(|\mathbf{r}_1|+|\mathbf{r}_2|)} F\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}. \tag{2.25}$$

Lastly, if f is real-valued, then so is T.

The properties of the functions ϕ_n upon which our numerical method is based, are collected in the following theorem, proved in Section 4.2.

Theorem 2.2. *Let $((C_n, \phi_n))_{n\in\mathbb{N}^*}$ be the unique solution in $(\mathbb{R} \times H^2(\mathbb{R}^3 \times \mathbb{R}^3))_{n\in\mathbb{N}^*}$ to the Rayleigh–Schrödinger system (2.9). Then, $\phi_1 = \phi_2 = 0$, $C_n = 0$ for $1 \leq n \leq 5$ and for each $n \geq 3$, there exists a positive integer N_n such that*

$$\phi_n = \sum_{(l_1,l_2)\in\mathcal{L}_n} \frac{1}{r_1 r_2} \left(\sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} T_{(l_1,l_2,m)}^{(n)}(r_1, r_2) Y_{l_1}^{m}(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2) \right), \tag{2.26}$$

where $\mathcal{L}_n$ is a finite subset of $\mathbb{N}^2$ with cardinality $N_n < \infty$, where $T_{(l_1,l_2,m)}^{(n)}$ is the unique solution to (2.19) in $H^1(\Omega)$ (or in $\widetilde{H}^1(\Omega)$ if $l_1 = l_2 = m = 0$) for $f = f_{(l_1,l_2,m)}^{(n)}$, where $f_{(l_1,l_2,m)}^{(n)}$ is a real-valued function that can be computed recursively from the $T_{(l_1',l_2',m')}^{(n')}$'s, for $n' < n$ (as in (4.13)). Moreover, there exists $\alpha_n > 0$ such that

$$\|e^{\alpha_n(r_1+r_2)} T_{(l_1,l_2,m)}^{(n)}\|_{H^1(\Omega)} < \infty, \tag{2.27}$$

$$\|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)} \phi_n\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} < \infty. \tag{2.28}$$

The number $N_n = |\mathcal{L}_n|$ (number of terms in the expansion) for $6 \le n \le 9$ are displayed in Table 2.1, whose construction rules are given in the proof of Theorem 2.2 (see Section 4.2). For $3 \le n \le 5$, $\mathcal{L}_n = B_n$, where the latter set is defined in (2.16), and $N_n = |B_n| = n-2$. For general n, $B_n \subset \mathcal{L}_n$. For $n \ge 6$, additional terms appear, as indicated in Table 2.1.

n	N_n	pairs of angular momentum quantum numbers (l_1, l_2) in $\mathcal{L}_n \backslash B_n$
6	8	(0,2;0,2)
7	13	(0,2;1,3), (1,3;0,2)
8	18	(0,2;0,2,4), (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 2.1: *Additional spherical harmonics appearing in each ϕ_n for $6 \le n \le 9$. N_n is the number of terms in the spherical harmonics expansion (2.26). The condensed notation $(l_1, l_1'; l_2, l_2')$ (resp. $(l_1, l_1'; l_2, l_2', l_2'')$ or $(l_1, l_1', l_1''; l_2, l_2')$) stands for the four (resp. six) pairs (l_1, l_2), (l_1', l_2), (l_1, l_2'), etc.*

Table 2.1 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 $Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2)$ might appear with a non-zero function $T^{(n)}_{(l_1,l_2,m)}$ in the spherical harmonics expansion (2.26) of ϕ_n. Conversely, if a given (l_1, l_2) does not appear in the table, then

$$\left\langle \phi_n, \frac{v(r_1, r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) \right\rangle = 0,$$

for all m_1, m_2 and all $v \in L^2(\Omega)$. The relative complexity of Table 2.1 is due to fact the first term in the right-hand side of (2.9) is a sum of bilinear terms in $\mathcal{B}^{(k)}$ and ϕ_{n-k}. The angular parts of both $\mathcal{B}^{(k)}$ and ϕ_{n-k} are finite linear combinations of angular basis functions $Y_{l_1}^m \otimes Y_{l_2}^{-m}$. When multiplied, they give rise to a still finite but longer linear combination of $Y_{l_1}^m \otimes Y_{l_2}^{-m}$'s (see (4.11)). By contrast, the corresponding table for the $\mathcal{B}^{(n)}$'s is quite simple, since all the rows have the same structure: for all $n \ge 3$, we have

$$n \quad | \quad n-2 \quad | \quad (k, n-k) \qquad \text{for } 1 \le k \le n-2. \tag{2.29}$$

From $(\phi_k)_{0 \le k \le n}$, 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_0 with each side of (2.9) and use the fact that $\langle \phi_0, (H_0 - \lambda_0)\phi_n \rangle = \langle (H_0 - \lambda_0)\phi_0, \phi_n \rangle = 0$. Since $(C_1, \phi_1) = (C_2, \phi_2) = 0$, we thus obtain

$$C_n = -\sum_{k=3}^{n-3} \left\langle \phi_0, \mathcal{B}^{(k)} \phi_{n-k} \right\rangle - \sum_{k=3}^{n-3} C_k \left\langle \phi_0, \phi_{n-k} \right\rangle, \tag{2.30}$$

where we use the convention $\sum_{k=m}^{n} \dots = 0$ if $m > n$. It follows that $C_3 = C_4 = C_5 = 0$.

Using (2.14), (2.26) and the orthonormality properties of the complex spherical harmonics, the terms $\left\langle \psi_0, \mathcal{B}^{(k)} \phi_{n-k} \right\rangle$ in (2.30) can be written as

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

$$\sum_{(l_1',l_2')\in\mathcal{L}_{n-k}} \frac{1}{r_1r_2} \sum_{m'=-\min(l_1',l_2')}^{\min(l_1',l_2')} T^{(n-k)}_{(l_1',l_2',m')}(r_1,r_2) Y_{l_1'}^{m'}(\theta_1,\phi_1) Y_{l_2'}^{-m'}(\theta_2,\phi_2)\Big\rangle$$
$$= - \sum_{(l_1,l_2)\in\mathcal{L}_{n-k}\cap B_k} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \beta^{(n-k)}_{(l_1,l_2,m)} t^{(n-k)}_{l_1,l_2,m}, \tag{2.31}$$

where

$$\beta^{(n)}_{(l_1,l_2,m)} := -\pi^{-1} G_c(l_1,l_2,m) \tag{2.32}$$
$$t^{(n)}_{(l_1,l_2,m)} := \int_\Omega r_1^{l_1+1} r_2^{l_2+1} e^{-(r_1+r_2)} T^{(n)}_{(l_1,l_2,m)}(r_1,r_2)\, dr_1\, dr_2, \tag{2.33}$$

with the convention that $t^{(n)}_{(l_1,l_2,m)} = 0$ if $(l_1,l_2) \notin \mathcal{L}_n$. In view of Table 2.1, we see in particular that since the sum in (2.31) is empty

$$\langle \phi_0, \mathcal{B}^{(k)}\phi_n \rangle = 0 \quad \forall\, k,n = 3,4,5,\ k \neq n, \tag{2.34}$$

and that many other vanish, e.g.

$$\langle \phi_0, \mathcal{B}^{(3)}\phi_6 \rangle = 0, \quad \langle \phi_0, \mathcal{B}^{(4)}\phi_5 \rangle = 0, \quad \langle \phi_0, \mathcal{B}^{(5)}\phi_4 \rangle = 0, \quad \langle \phi_0, \mathcal{B}^{(6)}\phi_3 \rangle = 0. \tag{2.35}$$

Additional pairs k, n can be examined by comparing the sets B_k and $\mathcal{L}_{n-k}$.

Furthermore, if the chosen numerical method to solve the boundary value problem (2.19) giving the radial function $T^{n-k}_{l_1',l_2',m'}$ 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 $t^{(n)}_{l_1,l_2,m}$ can be done explicitly, at least for the approximate solution [33, Section 7.3]. Using the fact that

$$\phi_0 = 4e^{-(r_1+r_2)} Y_0^0(\theta_1,\phi_1) Y_0^0(\theta_2,\phi_2), \tag{2.36}$$

we then have

$$\langle \phi_0, \phi_n \rangle = \Big\langle 4e^{-(r_1+r_2)} Y_0^0(\theta_1,\phi_1) Y_0^0(\theta_2,\phi_2),$$
$$\sum_{(l_1',l_2')\in\mathcal{L}_n} \frac{1}{r_1r_2} \sum_{m'=-\min(l_1',l_2')}^{\min(l_1',l_2')} T^{(n)}_{(l_1',l_2',m')}(r_1,r_2) Y_{l_1'}^{m'}(\theta_1,\phi_1) Y_{l_2'}^{-m'}(\theta_2,\phi_2)\Big\rangle$$
$$= 4t^{(n)}_{(0,0,0)}. \tag{2.37}$$

As a consequence, $\langle \phi_0, \phi_n \rangle = 0$ if $(0,0) \notin \mathcal{L}_n$, so that in particular

$$\langle \phi_0, \phi_3 \rangle = \langle \phi_0, \phi_4 \rangle = \langle \phi_0, \phi_5 \rangle = 0. \tag{2.38}$$

Then, C_n can be computed from (2.30) as

$$C_n = \sum_{k=3}^{n-3} \sum_{\substack{(l_1,l_2)\in\mathcal{L}_{n-k} \\ l_1+l_2=k-1 \\ l_1,l_2\neq 0}} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \beta^{(n-k)}_{(l_1,l_2,m)} t^{(n-k)}_{(l_1,l_2,m)} - 4\sum_{k=6}^{n-3} C_k t^{(n-k)}_{(0,0,0)}. \tag{2.39}$$

2.3. Practical computation of the lowest order terms. We detail in this section the practical computation of ϕ_3 (already done in [13]), ϕ_4 and ϕ_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 ϕ_3. We have

$$\mathcal{B}^{(3)} = r_1 r_2 \left(\sum_{m=-1}^{1} G_{\mathrm{c}}(1,1,m)) Y_1^m(\theta_1,\phi_1) Y_1^{-m}(\theta_2,\phi_2) \right), \tag{2.40}$$

$$(H_0 - \lambda_0)\phi_3 = -\mathcal{B}^{(3)}\phi_0, \tag{2.41}$$

$$\langle \phi_0, \phi_3 \rangle = 0, \tag{2.42}$$

with $G_{\mathrm{c}}(1,1,m) = -\frac{\pi}{3}(8 - 4|m|)$ and therefore

$$(H_0 - \lambda_0)\phi_3 = -r_1 r_2 e^{-(r_1+r_2)} \left(\sum_{m=-1}^{1} \pi^{-1} G_{\mathrm{c}}(1,1,m) Y_1^m(\theta_1,\phi_1) Y_1^{-m}(\theta_2,\phi_2) \right),$$

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

As a consequence, using Lemma 2.2, it holds that $\mathcal{L}_3 = \{(1,1)\}$,

$$\phi_3 = \frac{T_{(1,1)}^{(3)}(r_1,r_2)}{r_1 r_2} \left(\sum_{m=-1}^{1} \alpha_{(1,1,m)}^{(3)} Y_1^m(\theta_1,\phi_1) Y_1^{-m}(\theta_2,\phi_2) \right), \tag{2.43}$$

where $\alpha_{(1,1,m)}^{(3)} = -\pi^{-1} G_{\mathrm{c}}(1,1,m) = -\frac{1}{3}(8-4|m|)$ and where $T_{(1,1)}^{(3)} \in H_0^1(\Omega)$ can be numerically computed by solving the 2D boundary value problem

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

with homogeneous Dirichlet boundary conditions.

Computation of ϕ_4. To compute the next order, we first expand $\mathcal{B}^{(4)}$ as

$$\begin{aligned}\mathcal{B}^{(4)} =& r_1 r_2^2 \sum_{m=-1}^{1} G_{\mathrm{c}}(1,2,m) Y_1^m(\theta_1,\phi_1) Y_2^{-m}(\theta_2,\phi_2) \\ &+ r_1^2 r_2 \sum_{m=-2}^{2} G_{\mathrm{c}}(2,1,m) Y_1^m(\theta_1,\phi_1) Y_2^{-m}(\theta_2,\phi_2),\end{aligned}$$

with $G_{\mathrm{c}}(1,2,1) = G_{\mathrm{c}}(1,2,-1) = 4\pi/\sqrt{5}$, $G_{\mathrm{c}}(1,2,0) = 4\pi\sqrt{3}/\sqrt{5}$, $G_{\mathrm{c}}(2,1,m) = -G_{\mathrm{c}}(1,2,m)$. From (2.9)-(2.10), we get

$$(H_0 - \lambda_0)\phi_4 = -\mathcal{B}^{(3)}\phi_1 - \mathcal{B}^{(4)}\phi_0,$$
$$\langle \phi_0, \phi_4 \rangle = 0,$$

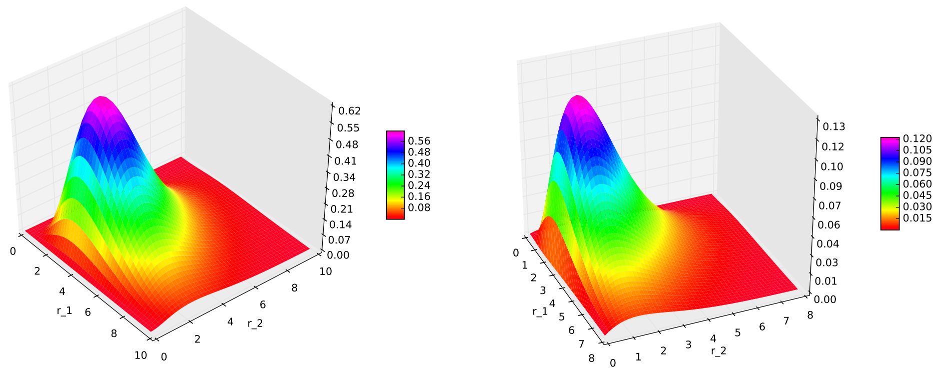
since $\phi_1 = \phi_2 = 0$ and $C_k = 0$ for $1 \leq k \leq 5$. We therefore have $\mathcal{L}_4 = \{(1,2),(2,1)\}$ and

$$\begin{aligned}\phi_4 =& \frac{T_{(1,2)}^{(4)}(r_1,r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha_{(1,2,m)}^{(4)} Y_1^m(\theta_1,\phi_1) Y_2^{-m}(\theta_2,\phi_2) \\ &+ \frac{T_{(2,1)}^{(4)}(r_1,r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha_{(2,1,m)}^{(4)} Y_2^m(\theta_1,\phi_1) Y_1^{-m}(\theta_2,\phi_2),\end{aligned}$$

where $\alpha^{(4)}_{(l_1,l_2,m)} = -\pi^{-1} G_c(l_1, l_2, m)$, $T^{(4)}_{(2,1)} \in H^1_0(\Omega)$ solves

$$-\frac{1}{2}\Delta_2 T^{(4)}_{(2,1)}(r_1, r_2) + (\kappa_2(r_1) + \kappa_1(r_2))\, T^{(4)}_{(2,1)} = r_1^3 r_2^2 e^{-r_1-r_2} \quad \text{in } \Omega, \tag{2.44}$$

and $T^{(4)}_{(1,2)}(r_1, r_2) = T^{(4)}_{(2,1)}(r_2, r_1)$. A representation of $T^{(4)}_{(2,1)}$ can be seen in Figure 2.1.



(a) (b)

Fig. 2.1: *Shape of* $T^{(4)}_{(2,1)}$ *(a) and* $T^{(4)}_{(2,1)}(r_1, r_2)/(r_1 r_2)$ *(b), using the Laguerre function approximation scheme [33, Section 7.3].*

Computation of ϕ_5. We have

$$\begin{aligned}\mathcal{B}^{(5)} =& r_1 r_2^3 \sum_{m=-1}^{1} G_c(1,3,m) Y_1^m(\theta_1,\phi_1) Y_3^{-m}(\theta_2,\phi_2)\\ &+ r_1^2 r_2^2 \sum_{m=-2}^{2} G_c(2,2,m) Y_2^m(\theta_1,\phi_1) Y_2^{-m}(\theta_2,\phi_2)\\ &+ r_1^3 r_2^1 \sum_{m=-1}^{1} G_c(3,1,m) Y_3^m(\theta_1,\phi_1) Y_1^{-m}(\theta_2,\phi_2),\end{aligned}$$

and

$$\begin{aligned}(H_0 - \lambda_0)\phi_5 &= -\mathcal{B}^{(5)}\phi_0,\\ \langle \phi_0, \phi_5 \rangle &= 0,\end{aligned}$$

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

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

$$+\frac{T^{(5)}_{(3,1)}(r_1,r_2)}{r_1 r_2}\sum_{m=-1}^{1}\alpha^{(5)}_{(3,1,m)}Y_3^m(\theta_1,\phi_1)Y_1^{-m}(\theta_2,\phi_2), \tag{2.45}$$

where $\alpha^{(5)}_{(l_1,l_2,m)} = -\pi^{-1}G_c(l_1,l_2,m)$, $T^{(5)}_{(1,3)} \in H_0^1(\Omega)$ solves

$$-\frac{1}{2}\Delta_2 T^{(5)}_{(1,3)}(r_1,r_2) + (\kappa_1(r_1)+\kappa_3(r_2))\,T^{(5)}_{(1,3)} = r_1^2 r_2^4 e^{-(r_1+r_2)}, \tag{2.46}$$

$T^{(5)}_{(2,3)} \in H_0^1(\Omega)$ solves

$$-\frac{1}{2}\Delta_2 T^{(5)}_{(2,2)}(r_1,r_2) + (\kappa_2(r_1)+\kappa_2(r_2))\,T^{(5)}_{(2,2)} = r_1^3 r_2^3 e^{-(r_1+r_2)}, \tag{2.47}$$

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

Computation of λ_n for $6 \le n \le 11$. Let us define for $n = 3,4,5$,

$$\beta^{(n)}_{(l_1,l_2)} := -\pi^{-1}\sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)}\alpha^{(n)}_{(l_1,l_2,m)}G_c(l_1,l_2,m)$$

$$t^{(n)}_{(l_1,l_2)} := \int_\Omega r_1^{l_1+1}r_2^{l_2+1}e^{-(r_1+r_2)}T^{(n)}_{(l_1,l_2)}(r_1,r_2)\,dr_1\,dr_2,$$

with the convention that $\beta^{(n)}_{(l_1,l_2)} = t^{(n)}_{(l_1,l_2)} = 0$ if $(l_1,l_2) \notin \mathcal{L}_n$. From (2.30) and the fact that $C_n = 0$ for $3 \le n \le 5$, we obtain, using (2.31), (2.38), (2.39), Table 2.1, and the symmetries of the coefficients $\beta^{(n)}_{(l_1,l_2)}$ and $t^{(n)}_{(l_1,l_2)}$,

$$\begin{aligned}
C_6 &= -\langle\phi_0,\mathcal{B}^{(3)}\phi_3\rangle = \beta^{(3)}_{(1,1)}t^{(3)}_{(1,1)}, \qquad (2.48)\\
C_7 &= -\langle\phi_0,\mathcal{B}^{(3)}\phi_4\rangle - \langle\phi_0,\mathcal{B}^{(4)}\phi_3\rangle = 0,\\
C_8 &= -\langle\phi_0,\mathcal{B}^{(3)}\phi_5\rangle - \langle\phi_0,\mathcal{B}^{(4)}\phi_4\rangle - \langle\phi_0,\mathcal{B}^{(5)}\phi_3\rangle = -\langle\phi_0,\mathcal{B}^{(4)}\phi_4\rangle\\
&= \beta^{(4)}_{(1,2)}t^{(4)}_{(1,2)} + \beta^{(4)}_{(2,1)}t^{(4)}_{(2,1)} = 2\beta^{(4)}_{(1,2)}t^{(4)}_{(1,2)},\\
C_9 &= -\langle\phi_0,\mathcal{B}^{(3)}\phi_6\rangle - \langle\phi_0,\mathcal{B}^{(4)}\phi_5\rangle - \langle\phi_0,\mathcal{B}^{(5)}\phi_4\rangle - \langle\phi_0,\mathcal{B}^{(6)}\phi_3\rangle - C_6\langle\phi_0,\phi_3\rangle = 0,\\
C_{10} &= -\sum_{k=3}^{7}\langle\phi_0,\mathcal{B}^{(k)}\phi_{10-k}\rangle - \sum_{k=6}^{7}C_k\langle\phi_0,\phi_{10-k}\rangle = -\langle\phi_0,\mathcal{B}^{(5)}\phi_5\rangle\\
&= \beta^{(5)}_{(1,3)}t^{(5)}_{(1,3)} + \beta^{(5)}_{(2,2)}t^{(5)}_{(2,2)} + \beta^{(5)}_{(3,1)}t^{(5)}_{(3,1)} = 2\beta^{(5)}_{(1,3)}t^{(5)}_{(1,3)} + \beta^{(5)}_{(2,2)}t^{(5)}_{(2,2)}, \qquad (2.49)\\
C_{11} &= -\sum_{k=3}^{8}\langle\phi_0,\mathcal{B}^{(k)}\phi_{11-k}\rangle - \sum_{k=6}^{8}C_k\langle\phi_0,\phi_{11-k}\rangle = -\langle\phi_0,\mathcal{B}^{(4)}\phi_7\rangle - \langle\phi_0,\mathcal{B}^{(5)}\phi_6\rangle\\
&= \sum_{m=-1}^{1}\left[\beta^{(7)}_{(1,2,m)}t^{(7)}_{(1,2,m)} + \beta^{(7)}_{(2,1,m)}t^{(7)}_{(2,1,m)}\right] + \sum_{m=-2}^{2}\beta^{(6)}_{(2,2,m)}t^{(6)}_{(2,2,m)}. \qquad (2.50)
\end{aligned}$$

As $\alpha^{(n)}_{(l_1,l_2,m)} = -\pi^{-1}G_c(l_1,l_2,m)$ for $n = 3,4,5$, $(l_1,l_2) \in \mathcal{L}_n$ and $-\min(l_1,l_2) \le m \le \min(l_1,l_2)$, we obtain, using (2.17), that

$$\left(\alpha^{(n)}_{(l_1,l_2,m)}\right)^2 = \frac{16\,((l_1+l_2)!)^2}{(2l_1+1)(2l_2+1)(l_1-m)!(l_1+m)!(l_2-m)!(l_2+m)!},$$

and therefore

$$\beta^{(3)}_{(1,1)} = \sum_{m=-1}^{1} (\alpha^{(3)}_{(1,1,m)})^2 = \frac{16}{9} + \frac{64}{9} + \frac{16}{9} = \frac{32}{3},$$

$$\beta^{(4)}_{(1,2)} = \beta^{(4)}_{(2,1)} = \sum_{m=-1}^{1} (\alpha^{(4)}_{(1,2,m)})^2 = \frac{16}{5} + 3 \times \frac{16}{5} + \frac{16}{5} = 16,$$

$$\beta^{(5)}_{(1,3)} = \beta^{(5)}_{(3,1)} = \sum_{m=-1}^{1} (\alpha^{(5)}_{(1,3,m)})^2 = \frac{64}{3}, \qquad \beta^{(5)}_{(2,2)} = \sum_{m=-2}^{2} (\alpha^{(5)}_{(2,2,m)})^2 = \frac{224}{5},$$

so that

$$C_6 = \frac{32}{3} t^{(3)}_{(1,1)}, \quad C_7 = 0, \quad C_8 = 32 t^{(4)}_{(1,2)}, \quad C_9 = 0, \qquad C_{10} = \frac{128}{3} t^{(5)}_{(1,3)} + \frac{224}{5} t^{(5)}_{(2,2)}. \tag{2.51}$$

It is optimal to use (2.51) to compute C_6, C_8, C_{10} since only ϕ_n is needed to compute C_{2n}. On the other hand, computing C_{11} using (2.50) requires computing ϕ_6 and ϕ_7, and it is therefore preferable to use Wigner's $(2n+1)$ rule that allows computing C_{11} from ϕ_3, ϕ_4 and ϕ_5.

Computation of higher-order terms. For $n \geq 6$, the right-hand side of (2.9) contains terms of the form $\mathcal{B}^{(k)}\phi_{n-k}$ with $k \geq 3$ and $n-k \geq 1$. The computation of ϕ_n therefore requires solving 2D boundary value problems of the form

$$-\frac{1}{2}\Delta T + (\kappa_{l_1}(r_1) + \kappa_{l_2}(r_2))\, T = r_1^{l'_1} r_2^{l'_2} T^{(n-k)}_{(l''_1,l''_2,m'')}$$

for some $(l_1,l_2) \in \mathcal{L}_n$, $l'_1 + l'_2 = k-1$, $(l''_1,l''_2) \in \mathcal{L}_{n-k}$ and $-\min(l''_1,l''_2) \leq m'' \leq \min(l''_1,l''_2)$. The right-hand side of this equation is not explicit, but the above equation can nevertheless be solved numerically since $T^{(n-k)}_{(l''_1,l''_2,m'')}$ has been previously computed numerically during the calculation of ϕ_{n-k}. An analogous procedure was used by Morgan and Simon for H_2^+ and can be found in the Appendix of [27].

3. Numerical results

3.1. Comparison between different approaches.

Tables 3.1, 3.2, and 3.3 contain the results of the approximated values of the C_n coefficients computed by Ovsiannikov and Mitroy [28], by Choy [15], by Pauling and Beach [29], and by the techniques described in this paper. The latter consist in solving recursively the Modified Slater–Kirkwood boundary value problems of type (2.9) using a Galerkin scheme in finite-dimensional approximation spaces constructed from tensor products of 1D Laguerre functions with degrees lower or equal to k. With basic double-precision floating-point arithmetics, the latter approach is numerically 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 [15] is based on the Slater–Kirkwood algorithm [34], whereas the method of Pauling and Beach [29] is different. Although Slater and Kirkwood are referenced in [29], Pauling and Beach were motivated by a method of S.C. Wang [39].

Method	C_6	C_8	C_{10}	C_{11}
[29]	6.49903	124.399	1135.21	
[15]	6.4990267	124.3990835	1135.2140398	
This work	6.49902670540 [13]	124.399083	3285.82841	-3474.89803
[28]	6.499026705406	124.3990835836	3285.828414967	-3474.898037882

Table 3.1: *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 (2.19) 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 [14, 26, 28, 35, 41].*

The discrepancy between the Choy [15] and Pauling–Beach [29] results (which agree to the digits given) and the other methods for C_{10} has the following origin. According to (2.49), 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 [15], who also was guided by [34], only computed the second term

$$\beta^{(5)}_{(2,2)} t^{(5)}_{(2,2)} = 1135.214\ldots \tag{3.1}$$

Method	C_{12}	C_{13}	C_{14}	C_{15}
This work	122727.608	-326986.924	6361736.04	-28395580.6
[28]	122727.6087007	-326986.9240441	6361736.045092	-28395580.6

Table 3.2: *Comparison of the C_n coefficients C_{12} to C_{15} between [28] and our method based on numerical solutions of boundary value problems of type (2.19) 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 [26, 28, 41] for C_{13} and C_{15} and [26, 28] 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
[28]	441205192.2739	-2.739281653140	3.93524773346	-3.07082459389

Table 3.3: *Comparison of the C_n coefficients C_{16} to C_{19} between [28] and our method based on numerical solutions of boundary value problems of type (2.19) 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 [26, 28].*

3.2. Role of continuous spectra in sum-over-state formulae. It follows from (2.41), (2.42) and (2.48) that the leading coefficient C_6 of the van der Waals expansion can be written as

$$C_6 = \langle \mathcal{B}^{(3)}\phi_0, (H_0 - \lambda_0)^{-1}_{\phi_0^\perp} \mathcal{B}^{(3)}\phi_0 \rangle,$$

where $(H_0 - \lambda_0)^{-1}_{\phi_0^\perp}$ is the inverse of the restriction to $H_0 - \lambda_0$ to the invariant subspace $\phi_0^\perp$ (which is well-defined since λ_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

$$C_6 = \sum_j \frac{|\langle \psi_j, \mathcal{B}^{(3)}\psi_0\rangle|^2}{E_j - E_0} \quad \text{(wrong)}, \tag{3.2}$$

with $\psi_0 := \phi_0$, $E_0 := \lambda_0 = -1$, where the ψ_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 (3.2) 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

$$C_6' := \sum_j \frac{|\langle \psi_j, \mathcal{B}^{(3)}\psi_0\rangle|^2}{E_j - E_0} = -\langle \mathcal{B}^{(3)}\phi_0, \phi_{3,\mathrm{pp}}\rangle,$$

where $\phi_{3,\mathrm{pp}}$ is the projection of ϕ_3 on the Hilbert space spanned by the eigenfunctions of H_0. Recall that the eigenvalues and associated eigenfunctions of the hydrogen atom Hamiltonian $h_0 := -\frac{1}{2}\Delta - \frac{1}{|\mathbf{r}|}$, which is a self-adjoint operator on $L^2(\mathbb{R}^3)$, are of the form

$$\varepsilon_n = -\frac{1}{2n^2}, \quad \psi_{n,l,m}(\mathbf{r}) = \varphi_{n,l}(r)Y_l^m(\theta,\phi), \quad n \in \mathbb{N}^*, \quad 0 \le l \le n-1, \quad -l \le m \le l, \tag{3.3}$$

with

$$\varphi_{n,1} = \sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-2)!}{2n(n+1)!}} \left(\frac{2r}{n}\right) L_{n-2}^{(3)}\left(\frac{2r}{n}\right) e^{-r/n}, \tag{3.4}$$

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

$$L_n^{(m)}(x) = (-1)^m \frac{\mathrm{d}^m L_{n+m}}{\mathrm{d}x^m}(x) = \frac{1}{n!}\sum_{k=0}^{n} \frac{n!}{k!}\binom{n+m}{n-k}(-x)^k. \tag{3.5}$$

The eigenvalues and associated eigenfunctions of H_0 are therefore given by

$$\mathcal{E}_{n_1,n_2} = \varepsilon_{n_1} + \varepsilon_{n_2} = -\frac{1}{2n_1^2} - \frac{1}{2n_2^2}, \qquad \Psi_{n_1,l_1,m_1;n_2,l_2,m_2} = \psi_{n_1,l_1,m_1} \otimes \psi_{n_2,l_2,m_2},$$

for $n_j \in \mathbb{N}^*$, $0 \le l_j \le n_j - 1$, $-l_j \le m_j \le l_j$. Note that $\phi_0 = \Psi_{1,0,0;1,0,0}$. We therefore have

$$C_6' = \sum_{(n_1,n_2)\in(\mathbb{N}^*\times\mathbb{N}^*)\setminus\{(1,1)\}} \sum_{l_1=0}^{n_1-1}\sum_{l_2=0}^{n_2-1}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2} \frac{|\langle \Psi_{n_1,l_1,m_1;n_2,l_2,m_2}, \mathcal{B}^{(3)}\psi_0\rangle|^2}{\varepsilon_{n_1}+\varepsilon_{n_2}+1}.$$

Using (2.40) and the $L^2(\mathbb{S}^2)$-orthonormality of the spherical harmonics, we get

$$\langle \Psi_{n_1,l_1,m_1;n_2,l_2,m_2}, \mathcal{B}^{(3)}\psi_0\rangle = \pi^{-1} S_{n_1} S_{n_2} \sum_{m=-1}^{1} G_{\mathrm{c}}(1,1,m)\delta_{l_1,1}\delta_{l_2,1}\delta_{m,m_1}\delta_{-m,m_2},$$

where

$$S_n := \int_0^{+\infty} r^3 e^{-r}\phi_{n,1}(r)\,\mathrm{d}r = 8n^3 \frac{(n-1)^{n-3}}{(n+1)^{n+3}}\sqrt{\frac{(n+1)!}{(n-2)!}}. \tag{3.6}$$

The latter expression is derived in Appendix C. We finally obtain

$$C_6' = \pi^{-2} \sum_{m=-1}^{1} |G_c(1,1,m)|^2 \sum_{n_1,n_2 \geq 2} \frac{S_{n_1}^2 S_{n_2}^2}{1 - \frac{1}{2n_1^2} - \frac{1}{2n_2^2}} = \frac{32}{3} \sum_{n_1,n_2 \geq 2} \frac{S_{n_1}^2 S_{n_2}^2}{1 - \frac{1}{2n_1^2} - \frac{1}{2n_2^2}}. \quad (3.7)$$

Summing up the terms of the above series for $n_1, n_2 \leq 300$ (note that $S_n \sim_{n\to\infty} \frac{8}{e^2 n^{3/2}}$), 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 2.2.

4.1. Proof of Lemma 2.2. Recall that the Hydrogen atom Hamiltonian $h_0 = -\frac{1}{2}\Delta - \frac{1}{|\mathbf{r}|}$ 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:

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

Since $H_0 = h_0 \otimes \mathbb{1}_{L^2(\mathbb{R}^3)} + \mathbb{1}_{L^2(\mathbb{R}^3)} \otimes h_0$, 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

$$H_0 \phi_0 = \lambda_0 \phi_0 \quad \text{with} \quad \phi_0 = \psi_{1,0,0} \otimes \psi_{1,0,0} = \pi^{-1} e^{-(r_1+r_2)},\ \|\phi_0\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} = 1 \text{ and } \lambda_0 = -1.$$

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

$$(H_0 - \lambda_0)\Psi = F - \mu \phi_0, \quad \langle \phi_0, \Psi \rangle = \alpha, \quad (4.1)$$

is well-posed and its unique solution is given by

$$\Psi = (H_0 - \lambda_0)|_{\phi_0^\perp}^{-1} \Pi_{\phi_0^\perp} F + \alpha \phi_0, \quad \mu = \langle \phi_0, F \rangle,$$

where $(H_0 - \lambda_0)|_{\phi_0^\perp}^{-1}$ 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

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

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

$$(\mathcal{U}(f \otimes s_1 \otimes s_2))(\mathbf{r}_1, \mathbf{r}_2) = \frac{f(|\mathbf{r}_1|, |\mathbf{r}_2|)}{|\mathbf{r}_1|\,|\mathbf{r}_2|}\, s_1\left(\frac{\mathbf{r}_1}{|\mathbf{r}_1|}\right) s_2\left(\frac{\mathbf{r}_2}{|\mathbf{r}_2|}\right).$$

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

$$L^2(\Omega) \otimes L^2(\mathbb{S}^2) \otimes L^2(\mathbb{S}^2) = \bigoplus_{l_1,l_2\in\mathbb{N}} \bigoplus_{m_1=-l_1}^{l_1} \bigoplus_{m_2=-l_2}^{l_2} \mathcal{H}_{l_1,l_2}^{m_1,m_2}$$

where $\mathcal{H}_{l_1,l_2}^{m_1,m_2} := L^2(\Omega)\otimes\mathbb{C}Y_{l_1}^{m_1}\otimes\mathbb{C}Y_{l_2}^{m_2}$. It follows from classical results for Schrödinger operators on $L^2(\mathbb{R}^3)$ with central potentials (see e.g. [31, Section XIII.3.B]) that each $\mathcal{H}_{l_1,l_2}^{m_1,m_2}$ is an invariant subspace for $\mathcal{U}^* H_0 \mathcal{U}$ and that

$$\mathcal{U}^* H_0 \mathcal{U}|_{\mathcal{H}_{l_1,l_2}^{m_1,m_2}} = H_{l_1,l_2} \otimes \mathbb{1}_{\mathbb{C}Y_{l_1}^{m_1}} \otimes \mathbb{1}_{\mathbb{C}Y_{l_2}^{m_2}},$$

where the expression of H_{l_1,l_2} can be derived by adapting the arguments in [13, Section 3], that we do not detail here for the sake of brevity: H_{l_1,l_2} is the self-adjoint operator on $L^2(\Omega)$ with form domain $H_1^0(\Omega)$ defined by

$$H_{l_1,l_2} = -\frac{1}{2}\Delta + \kappa_{l_1}(r_1) + \kappa_{l_2}(r_2) + \lambda_0. \tag{4.2}$$

Note that the operator H_{l_1,l_2} on $L^2(\Omega) \equiv L^2(0,+\infty)\otimes L^2(0,+\infty)$ can itself be decomposed as

$$H_{l_1,l_2} = h_{l_1} \otimes \mathbb{1}_{L^2(0,+\infty)} + \mathbb{1}_{L^2(0,+\infty)} \otimes h_{l_2} \geq -\frac{1}{2(l_1+1)^2} - \frac{1}{2(l_2+1)^2},$$

where for each $l \in \mathbb{N}$, h_l is the self-adjoint operator on $L^2(0,+\infty)$ with form domain $H_0^1(0,+\infty)$ defined by

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

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

$$H_{l_1,l_2} - \lambda_0 = H_{l_1,l_2} + 1 \geq \frac{3}{8} \quad \text{for all } (l_1,l_2) \in \mathbb{N}^2 \setminus \{(0,0\}. \tag{4.3}$$

Choosing $\alpha = 0$ in (4.1) amounts to enforcing that the solution Ψ is in $\phi_0^\perp$. Taking $\alpha = 0$ and $F = \frac{f(r_1,r_2)}{r_1 r_2} Y_{l_1}^{m_1}(\theta_1,\phi_1) Y_{l_2}^{m_2}(\theta_2,\phi_2) = \mathcal{U}(f \otimes Y_{l_1}^{m_1} \otimes Y_{l_2}^{m_2})$, with $f \in L^2(\Omega)$, it follows that (2.21) has a unique solution in $H^2(\mathbb{R}^3\times\mathbb{R}^3)$ if and only if $\mu = \langle \phi_0, F\rangle = 0$, that is

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

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

$$\begin{aligned} &T := (H_{l_1,l_2} - \lambda_0)^{-1} f && \text{if } (l_1,l_2) \neq (0,0), \\ &T := (H_{0,0} - \lambda_0)|^{-1}_{(r_1 r_2 e^{-(r_1+r_2)})^\perp} f && \text{if } (l_1,l_2) = (0,0). \end{aligned}$$

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 (2.19) in $H_0^1(\Omega)$ if $(l_1,l_2) \neq (0,0)$ and T is the unique solution to (2.19) in $\widetilde{H}_0^1(\Omega) = H_0^1(\Omega) \cap (r_1 r_2 e^{-(r_1+r_2)})^\perp$ if $(l_1,l_2) = 0$.

The fact that if f decays exponentially at infinity, then so does T, hence ψ, is a consequence of the following result, whose proof follows the same lines as in [13, Section 3.3] where this result is established for the special case when $(l_1, l_2) = (1, 1)$ and $f = r_1^2 r_2^2 e^{-(r_1+r_2)}$.

LEMMA 4.1. *If the function f of (2.19) decays exponentially at infinity at a rate $\eta > 0$, in the sense that*

$$\|e^{\eta(r_1+r_2)} f\|_{L^2(\Omega)} < \infty, \tag{4.4}$$

then the unique solution T of (2.19) also decays exponentially at infinity. More precisely, for all $0 \le \alpha < \sqrt{3/8}$, there exists a constant $C_\alpha \in \mathbb{R}_+$ such that for all $\eta > \alpha$ and all $f \in L^2(\Omega)$ satisfying (4.4), it holds

$$\|e^{\alpha(r_1+r_2)} T\|_{H^1(\Omega)} \le C_\alpha \|e^{\eta(r_1+r_2)} f\|_{L^2(\Omega)}. \tag{4.5}$$

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 $H_0^1(\Omega)$ by $\widetilde{H}_0^1(\Omega)$. Let a be the continuous bilinear form on $H_0^1(\Omega) \times H_0^1(\Omega)$ associated with the positive self-adjoint operator $H_{l_1,l_2} - \lambda_0$:

$$\forall u, v \in H_0^1(\Omega), \quad a(u, v) = \frac{1}{2} \int_\Omega \nabla u \cdot \nabla v + \int_\Omega (\kappa_{l_1}(r_1) + \kappa_{l_2}(r_2)) u(r_1, r_2) v(r_1, r_2)\, dr_1\, dr_2.$$

Recall that the continuity of a can be shown directly (without using the fact that $H_0^1(\Omega)$ is the form domain of $H_{l_1 l_2}$) as a straightforward consequence of the one-dimensional Hardy inequality

$$\forall g \in H_0^1(0, +\infty), \quad \int_0^\infty (g(r)/r)^2 \mathrm{d}r \le 4 \int_0^\infty g'(r)^2\, \mathrm{d}r. \tag{4.6}$$

It follows from (4.3) that $a \ge \frac{3}{8}$ (in the sense of quadratic forms on $L^2(\Omega)$). For $0 \le \alpha < \sqrt{3/8}$, we introduce the continuous bilinear form a_α on $H_0^1(\Omega) \times H_0^1(\Omega)$ defined by

$$\forall u, v \in H_0^1(\Omega), \quad a_\alpha(u, v) = a(u, v) - \int_\Omega \alpha u(\mathbf{r}) \left(\frac{\partial v}{\partial r_1}(\mathbf{r}) + \frac{\partial v}{\partial r_2}(\mathbf{r}) \right) \mathrm{d}\mathbf{r} - \int_\Omega \alpha^2 u(\mathbf{r}) v(\mathbf{r}) \mathrm{d}\mathbf{r},$$

for which

$$\forall v \in H_0^1(\Omega), \quad a_\alpha(v, v) = a(v, v) - \alpha^2 \|v\|_{L^2(\Omega)}^2 \ge \underbrace{\left(\frac{3}{8} - \alpha^2 \right)}_{>0} \|v\|_{L^2(\Omega)}^2.$$

Using either the fact that $\kappa_l(r) \ge \frac{1}{4}$ (for $l \ge 1$) or the Hardy inequality (4.6) (for $l = 0$), we also have

$$\forall v \in H_0^1(\Omega), \quad a_\alpha(v, v) = a(v, v) - \alpha^2 \|v\|_{L^2(\Omega)}^2 \ge \frac{1}{4} \int_\Omega |\nabla v|^2 - 2\|v\|_{L^2}^2.$$

Since $a \ge \frac{3}{8}$ and $a_\alpha \ge \left(\frac{3}{8} - \alpha^2\right) > 0$, the above bound implies that a and a_α are both continuous and coercive on $H_0^1(\Omega)$. The function $T \in H_0^1(\Omega)$ solution to (2.19) is also the unique solution to the variational equation

$$\forall w \in H_0^1(\Omega), \quad a(T, w) = \int_\Omega f w.$$

Proceeding as in [13, Section 3.3], we obtain that for all $u \in H^1_0(\Omega)$ such that $e^{\alpha(r_1+r_2)}u \in H^1_0(\Omega)$ and $w \in C^\infty_c(\Omega)$, we have

$$a_\alpha(e^{\alpha(r_1+r_2)}u, w) = a(u, e^{\alpha(r_1+r_2)}w). \tag{4.7}$$

Consider now $f \in L^2(\Omega)$ satisfying (4.4) 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 $\|v\|_{H^1(\Omega)} \le C_\alpha \|e^{\alpha(r_1+r_2)}f\|_{L^2(\Omega)} \le C_\alpha \|e^{\eta(r_1+r_2)}f\|_{L^2(\Omega)}$, where $C_\alpha \ge 1$ is the ratio between the continuity constant and the coercivity constant of a_α. Let $u = e^{-\alpha(r_1+r_2)}v \in H^1_0(\Omega)$. In view of (4.7), 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 $\|e^{\alpha(r_1+r_2)}T\|_{H^1(\Omega)} = \|e^{\alpha(r_1+r_2)}u\|_{H^1(\Omega)} = \|v\|_{H^1(\Omega)} \le C_\alpha \|e^{\eta(r_1+r_2)}f\|_{L^2(\Omega)}$. ∎

As a consequence, we have

$$\begin{aligned}\|e^{\alpha(|\mathbf{r}_1|+|\mathbf{r}_2|)}\psi\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} &= \|e^{\alpha(r_1+r_2)}T\|_{L^2(\Omega)} \le \|e^{\alpha(r_1+r_2)}T\|_{H^1(\Omega)} \\ &\le C_\alpha \|e^{\eta(r_1+r_2)}f\|_{L^2(\Omega)} = C_\alpha \|e^{\eta(|\mathbf{r}_1|+|\mathbf{r}_2|)}F\|_{L^2(\mathbb{R}^6)},\end{aligned}$$

which proves (2.25). In addition, a simple calculation using (4.6) shows that for all $g \in H^1_0(\Omega)$

$$\begin{aligned}\left\| \frac{g}{r_1 r_2} \otimes Y^{m_1}_{l_1} \otimes Y^{m_2}_{l_2} \right\|^2_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} &= \|g\|^2_{H^1(\Omega)} + l_1(l_1+1) \left\| \frac{g}{r_1} \right\|^2_{L^2(\Omega)} + l_2(l_2+1) \left\| \frac{g}{r_2} \right\|^2_{L^2(\Omega)} \\ &\le (1 + 4l_1(l_1+1) + 4l_2(l_2+1)) \|g\|^2_{H^1},\end{aligned}$$

yielding

$$\begin{aligned}\|e^{\alpha(|\mathbf{r}_1|+|\mathbf{r}_2|)}\psi\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} &\le (1 + 4l_1(l_1+1) + 4l_2(l_2+1))^{1/2} \|e^{\alpha(r_1+r_2)}T\|_{H^1(\Omega)} \\ &\le C_\alpha (1 + 4l_1(l_1+1) + 4l_2(l_2+1))^{1/2} \|e^{\eta(|\mathbf{r}_1|+|\mathbf{r}_2|)}F\|_{L^2(\Omega)}.\end{aligned}$$

Lastly, since H_{l_1,l_2} is a real operator in the sense that $\overline{H_{l_1,l_2}\phi} = H_{l_1,l_2}\overline{\phi}$ for all $\phi \in D(H_{l_1,l_2})$, it is obvious that T is real-valued, whenever f is.

4.2. Proof of Lemma 2.1 and Theorem 2.2. We have seen in the previous section that for each $(\alpha, F) \in \mathbb{R} \times L^2(\mathbb{R}^3 \times \mathbb{R}^3)$, (4.1) has a unique solution (μ, ψ) 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 (2.9)-(2.10) is well-posed and that ϕ_n is of the form (2.26), we proceed by induction on n. It is proven in [13] that for $n = 3$,

$$\phi_3 = \frac{T^{(3)}_{(1,1)}(r_1, r_2)}{r_1 r_2} \sum_{m=-1}^{1} \alpha^{(3)}_{(1,1,m)} Y_1^m(\theta_1, \phi_1) Y_1^{-m}(\theta_2, \phi_2),$$

with $\alpha^{(3)}_{(1,1,m)} = -\pi G_c(1, 1, m)$ and $\|T^{(3)}_{(1,1)}(r_1, r_2) e^{\eta^3_{1,1}(r_1+r_2)}\|_{H_1(\Omega)} =: C^3_{1,1} < \infty$. 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 $3 \leq k \leq n$,

$$\phi_k = \sum_{(l_1,l_2)\in\mathcal{L}_k} \frac{1}{r_1 r_2} \left(\sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} T^{(k)}_{(l_1,l_2,m)}(r_1, r_2) Y^m_{l_1}(\theta_1, \phi_1) Y^{-m}_{l_2}(\theta_2, \phi_2) \right), \tag{4.8}$$

for some finite set $\mathcal{L}_k \subset \mathbb{N}^2$ with cardinality $N_k < \infty$, where $T^{(k)}_{(l_1,l_2,m)}$ is the unique solution to (2.19) in $H^1(\Omega)$ (or in $\widetilde{H}^1(\Omega)$ if $l_1 = l_2 = 0$) for $f = f^{(k)}_{(l_1,l_2,m)} \in L^2(\Omega)$ and that for all $(l_1, l_2) \in \mathcal{L}_k$ and $-\min(l_1, l_2) \leq m \leq \min(l_1, l_2)$ there exists $\eta^k_{l_1,l_2,m} > 0$ such that

$$\|T^{(k)}_{(l_1,l_2,m)}(r_1, r_2) e^{\eta^k_{l_1,l_2,m}(r_1+r_2)}\|_{H^1(\Omega)} =: C^k_{l_1,l_2,m} < \infty. \tag{4.9}$$

From (2.14), the fact that $\phi_1 = \phi_2 = 0$ and the recursion hypothesis (4.8), we obtain that for all $3 \leq k \leq n + 1$,

$$\mathcal{B}^{(k)}\phi_{n+1-k} = \sum_{\substack{l_1+l_2=k-1\\ l_1,l_2\neq 0}} \sum_{(l_1',l_2')\in\mathcal{L}_{n+1-k}} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \sum_{m'=-\min(l_1',l_2')}^{\min(l_1',l_2')} \mathcal{U}\left(f^{m,m'}_{n-k+1,l_1,l_1',l_2,l_2'} \otimes Y^m_{l_1} Y^{m'}_{l_1'} \otimes Y^{-m}_{l_2} Y^{-m'}_{l_2'} \right), \tag{4.10}$$

where

$$f^{m,m'}_{j,l_1,l_1',l_2,l_2'}(r_1, r_2) := G_c(l_1, l_2, m) r_1^{l_1} r_2^{l_2} T^{(j)}_{(l_1',l_2',m')}(r_1, r_2).$$

In addition, we have

$$Y^m_l Y^{m'}_{l'} = \sum_{l''=|l-l'|}^{l+l'} \zeta^{m,m'}_{l,l',l''} Y^{m+m'}_{l''}, \tag{4.11}$$

where the coefficients $\zeta^{m,m'}_{l,l',l''} \in \mathbb{R}$ can be computed explicitly using Wigner's 3-j symbols [12, p. 146]:

$$\zeta^{m,m'}_{l,l',l''} = (-1)^{m+m'} \sqrt{\frac{(2l + 1)(2l' + 1)(2l'' + 1)}{4\pi}} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ m & m' & -m - m' \end{pmatrix}.$$

In particular $\zeta^{m,m'}_{l,l',l''} = 0$ if $l + l' + l'' \notin 2\mathbb{N}$. This implies that

$$-\sum_{k=3}^{n+1} \mathcal{B}^{(k)}\phi_{n+1-k} - \sum_{k=1}^{n+1} C_k \phi_{n+1-k}$$

$$= \sum_{(l_1,l_2)\in\mathcal{L}_{n+1}} \frac{1}{r_1 r_2} \left(\sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} f^{(n+1)}_{(l_1,l_2,m)}(r_1,r_2) Y^m_{l_1}(\theta_1,\phi_1) Y^{-m}_{l_2}(\theta_2,\phi_2) \right), \quad (4.12)$$

for some $\mathcal{L}_{n+1} \subset \mathbb{N}^2$ with finite cardinality, where for $(l_1,l_2) \in \mathcal{L}_{n+1}$, $-\min(l_1,l_2) \leq m \leq \min(l_1,l_2)$,

$$f^{(n+1)}_{(l_1,l_2,m)} = -\sum_{k=3}^{n+1} \Bigg[C_k T^{(n-k+1)}_{(l_1,l_2,m)}(r_1,r_2) + \sum_{\substack{m',m''\geq 0\\ m'+m''=m}} \sum_{\substack{l'_1+l'_2=k-1\\ l'_1,l'_2\neq 0\\ \min(l'_1,l'_2)\geq |m'|}} \sum_{\substack{(l''_1,l''_2)\in\mathcal{L}_{n+1-k}\\ \min(l''_1,l''_2)\geq |m''|}} r_1^{l'_1} r_2^{l'_2} T^{(n-k+1)}_{(l''_1,l''_2,m'')}(r_1,r_2) G_c(l'_1,l'_2,m') \zeta^{m',m''}_{l'_1,l''_1,l_1} \zeta^{m',m''}_{l'_2,l''_2,l_2} \Bigg] \quad (4.13)$$

is a linear combination of the functions $r_1^{l'_1} r_2^{l'_2} T^{(j)}_{(l''_1,l''_2,m'')} \in L^2(\Omega)$, $3 \leq j \leq n$, $l''_1, l''_2 \in \mathcal{L}_j$, $l'_1 + l'_2 + j \leq n+1$, $-\min(l''_1,l''_2) \leq m'' \leq \min(l''_1,l''_2)$ and therefore satisfies in view of (4.9)

$$\|f^{(n+1)}_{(l_1,l_2,m)}(r_1,r_2) e^{\xi^{n+1}_{l_1,l_2,m}(r_1+r_2)}\|_{H_1(\Omega)} < \infty \quad (4.14)$$

for some $\xi^{n+1}_{l_1,l_2,m} > 0$. Therefore the problem consists of seeking $(C_{n+1},\phi_{n+1}) \in \mathbb{R} \times H^2(\mathbb{R}^3\times\mathbb{R}^3)$ satisfying

$$(H_0 - \lambda_0)\phi_{n+1} = -\sum_{k=3}^{n+1} \mathcal{B}^{(k)}\phi_{n+1-k}, -\sum_{k=1}^{n+1} C_k \phi_{n+1-k}, \;\; \langle \phi_0, \phi_{n+1}\rangle = -\frac{1}{2}\sum_{k=1}^{n} \langle \phi_k, \phi_{n+1-k}\rangle$$

is well-posed and we deduce from Lemma 2.2 that

$$\phi_{n+1} := \sum_{(l_1,l_2)\in\mathcal{L}_{n+1}} \frac{1}{r_1 r_2} \left(\sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} T^{(n+1)}_{(l_1,l_2,m)}(r_1,r_2) Y^m_{l_1}(\theta_1,\phi_1) Y^{-m}_{l_2}(\theta_2,\phi_2) \right),$$

where $T^{(n+1)}_{(l_1,l_2,m)}$ is the unique solution to (2.19) in $H^1(\Omega)$ (or in $\widetilde{H}^1(\Omega)$ if $l_1 = l_2 = 0$) for $f = f^{(n+1)}_{(l_1,l_2,m)}$. In addition, it follows from (4.14) that (4.9) holds true for $k = n+1$. Therefore, the Rayleigh–Schrödinger triangular system (2.9)-(2.10) is well-posed and the $T^{(n)}_{(l_1,l_2,m)}$'s decay exponentially at infinity in the sense of (4.9). From (4.8) we obtain that for

$$\alpha_n = \min_{\substack{(l_1,l_2)\in\mathcal{L}_n\\ -\min(l_1,l_2)\leq m\leq\min(l_1,l_2)}} (\eta^n_{l_1,l_2,m}) > 0,$$

we have

$$\|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_n\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} \leq C_n \sum_{(l_1,l_2)\in\mathcal{L}_n} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \|e^{\alpha_n(r_1+r_2)} T^{(n)}_{(l_1,l_2,m)}\|_{H^1(\Omega)}$$

$$\leq C_n \sum_{(l_1,l_2)\in\mathcal{L}_n} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} \|e^{\eta^n_{(l_1,l_2,m)}(r_1+r_2)} T^{(n)}_{(l_1,l_2,m)}\|_{H^1(\Omega)} < \infty,$$

for some $C_n \in \mathbb{R}_+$, so that ϕ_n decays exponentially at infinity in the sense of (2.28). Lastly, we infer from Wigner's $(2n+1)$ rule and the fact that $\phi_1 = \phi_2 = 0$, that $C_n = 0$ for $1 \le n \le 5$. This completes the proof of both Lemma 2.1 and Theorem 2.2.

Let us finally explain how to construct Table 2.1. We have already shown that $\mathcal{L}_3 = \{(1,1)\}$, and from (4.10)-(4.12) and the fact that $\phi_1 = \phi_2 = 0$, we see that

$$\mathcal{L}_{n+1} \subset \left(\bigcup_{k=3}^{n-2} \mathcal{M}_{k,n+1-k} \right) \bigcup \mathcal{M}_{n+1,0} \bigcup \left(\bigcup_{3 \le k \le n-5 \mid C_{n+1-k} \ne 0} \mathcal{L}_k \right),$$

where for $k, n \ge 3$,

$$\begin{aligned} \mathcal{M}_{k,0} &= \{(l_1,l_2) \in \mathbb{N}^* \times \mathbb{N}^* \mid l_1 + l_2 = k-1\} = \{(1,k-2), \cdots, (k-2,1)\}, \\ \mathcal{M}_{k,n} &= \big\{(l_1,l_2) \in \mathbb{N} \times \mathbb{N} \mid \exists (l_1', l_2') \in \mathcal{M}_{k,0},\ \exists (l_1'', l_2'') \in \mathcal{L}_n \text{ s.t.} \\ &\qquad |l_j' - l_j''| \le l_j \le l_j' + l_j'',\ l_j + l_j' + l_j'' \in 2\mathbb{N},\ j = 1,2 \big\}. \end{aligned}$$

Consequently, we have

$$\begin{aligned} &\mathcal{L}_4 = \mathcal{M}_{4,0}; \\ &\mathcal{L}_5 = \mathcal{M}_{5,0}; \\ &\mathcal{L}_6 = \mathcal{M}_{3,3} \cup \mathcal{M}_{6,0} \quad \text{with} \quad \mathcal{M}_{3,3} = \{(0,2;0,2)\}; \\ &\mathcal{L}_7 = \mathcal{M}_{3,4} \cup \mathcal{M}_{4,3} \cup \mathcal{M}_{7,0} \quad \text{with} \quad \mathcal{M}_{3,4} = \mathcal{M}_{4,3} = \{(0,2;1,3),(1,3;0,2)\}; \\ &\mathcal{L}_8 = \mathcal{M}_{3,5} \cup \mathcal{M}_{4,4} \cup \mathcal{M}_{5,3} \cup \mathcal{M}_{8,0} \quad \text{with} \\ &\qquad \mathcal{M}_{3,5} = \mathcal{M}_{5,3} = \{(0,2;2,4),(1,3;1,3),(2,4;0,2)\}, \\ &\qquad \mathcal{M}_{4,4} = \{(0,2;0,2,4),(0,2,4;0,2),(1,3;1,3)\} \\ &\mathcal{L}_9 = \mathcal{M}_{3,6} \cup \mathcal{M}_{4,5} \cup \mathcal{M}_{5,4} \cup \mathcal{M}_{6,3} \cup \mathcal{M}_{9,0} \cup \mathcal{L}_3 \quad \text{with} \\ &\qquad \mathcal{M}_{6,3} \subsetneq \mathcal{M}_{3,6} = \{(0,2;3,5),(1,3;2,4),(2,4;1,3),(3,5;0,2),(1,3;1,3)\}, \\ &\qquad \mathcal{M}_{4,5} = \mathcal{M}_{5,4} \\ &\qquad\qquad = \{(0,2;1,3,5),(1,3;0,2,4),(2,4;1,3),(1,3;2,4),(0,2,4;1,3),(1,3,5;0,2)\}, \end{aligned}$$

where we recall that $(l_1, l_1'; l_2, l_2')$ (resp. $(l_1, l_1'; l_2, l_2', l_2'')$, $(l_1, l_1', l_1''; l_2, l_2')$) 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 2.1.

4.3. Proof of Theorem 2.1. As in [13], we introduce the space

$$\mathcal{V} = \left\{ v \in L^2(\mathbb{R}^3 \times \mathbb{R}^3) \, : \, v(\mathbf{r}_1, \mathbf{r}_2) = v(\mathbf{r}_2, \mathbf{r}_1) \ \forall \mathbf{r}_1, \mathbf{r}_2 \in \mathbb{R}^3 \right\}, \tag{4.15}$$

the functions $\psi_\epsilon^{(n)} \in \mathcal{V} \cap H^2(\mathbb{R}^3 \times \mathbb{R}^3)$ normalized in $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$,

$$\psi_\epsilon^{(n)} := m_\epsilon^{(n)} \mathcal{T}_\epsilon \left(\phi_\epsilon^{(n)} \right) \text{ where } \phi_\epsilon^{(n)} := \phi_0 + \sum_{k=3}^n \epsilon^k \phi_k \text{ and } m_\epsilon^{(n)} = \left\| \mathcal{T}_\epsilon \left(\phi_\epsilon^{(n)} \right) \right\|_{L^2(\mathbb{R}^3 \times \mathbb{R}^3)}^{-1}, \tag{4.16}$$

as well as the Rayleigh quotient

$$\mu_\epsilon^{(n)} = \left\langle \psi_\epsilon^{(n)}, H_\epsilon \psi_\epsilon^{(n)} \right\rangle \tag{4.17}$$

and the approximation

$$\lambda_\epsilon^{(n)} = \lambda_0 - \sum_{k=6}^n C_n \epsilon^n$$

of λ_ϵ. When $\epsilon \to 0$, we have $\mathcal{T}_\epsilon(\phi_0) \to 1$ and therefore $m_\epsilon^{(n)} \to 1$. We know from [13, Section 2.4] that there exists a constant $C \in \mathbb{R}_+$ such that for $\epsilon > 0$ small enough

$$\|\psi_\epsilon - \psi_\epsilon^{(3)}\|_{H^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq C\epsilon^4, \quad |\lambda_\epsilon - \mu_\epsilon^{(3)}| \leq C\epsilon^8, \quad \text{and} \quad |\lambda_\epsilon - \lambda_\epsilon^{(6)}| \leq C\epsilon^7.$$

It follows from Theorem 2.2 that the ϕ_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

$$\|\psi_\epsilon - \psi_\epsilon^{(n)}\|_{H^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq c_n\epsilon^4.$$

We infer from [13, 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 $0 < \epsilon \leq \epsilon_n$,

$$|\lambda_\epsilon - \mu_\epsilon^{(n)}| \leq C\|H_\epsilon\psi_\epsilon^{(n)} - \mu_\epsilon^{(n)}\psi_\epsilon^{(n)}\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}, \tag{4.18}$$

$$\|\psi_\epsilon - \psi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq C\|H_\epsilon\psi_\epsilon^{(n)} - \mu_\epsilon^{(n)}\psi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \tag{4.19}$$

(the first estimate above follows from the Kato-Temple inequality [22]). To proceed further, we need to evaluate the L^2-norm of the residual $r_\epsilon^{(n)} := H_\epsilon\psi_\epsilon^{(n)} - \mu_\epsilon^{(n)}\psi_\epsilon^{(n)}$. We have

$$H_\epsilon\psi_\epsilon^{(n)} = m_\epsilon^{(n)}H_\epsilon\mathcal{T}_\epsilon(\phi_\epsilon^{(n)}) = m_\epsilon^{(n)}\mathcal{T}_\epsilon\left[(H_0+V_\epsilon)\phi_\epsilon^{(n)}\right] = m_\epsilon^{(n)}\mathcal{T}_\epsilon\left[(H_0+V_\epsilon)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k)\right],$$

and thus,

$$\begin{aligned}
r_\epsilon^{(n)} &= m_\epsilon^{(n)}\mathcal{T}_\epsilon\left[(H_0+V_\epsilon)\phi_\epsilon^{(n)} - \mu_\epsilon^{(n)}\phi_\epsilon^{(n)}\right] \\
&= m_\epsilon^{(n)}\mathcal{T}_\epsilon\Bigg[(H_0+V_\epsilon)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) - (\lambda_0 - \sum_{k=3}^n C_k\epsilon^k)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) \\
&\qquad + (\lambda_\epsilon^{(n)} - \mu_\epsilon^{(n)})\phi_\epsilon^{(n)}\Bigg] \\
&= m_\epsilon^{(n)}\mathcal{T}_\epsilon\Bigg[\left(H_0 + \sum_{k=3}^n \epsilon^k\mathcal{B}^{(k)}\right)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) - (\lambda_0 - \sum_{k=3}^n C_k\epsilon^k)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) \\
&\qquad + (\lambda_\epsilon^{(n)} - \mu_\epsilon^{(n)})\phi_\epsilon^{(n)} + (V_\epsilon - \sum_{k=3}^n \epsilon^k\mathcal{B}^{(k)})\phi_\epsilon^{(n)}\Bigg].
\end{aligned}$$

Using (2.9), we get

$$\begin{aligned}
&(H_0 + \sum_{k=3}^n \epsilon^k\mathcal{B}^{(k)})(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) - (\lambda_0 - \sum_{k=3}^n C_k\epsilon^k)(\phi_0 + \sum_{k=3}^n \epsilon^k\phi_k) \\
=&\epsilon^n \sum_{k=1}^n \epsilon^k\left(\sum_{j=k}^n \mathcal{B}^{(j)}\phi_{n+k-j} + \sum_{j=k}^n C_j\phi_{n+k-j}\right).
\end{aligned} \tag{4.20}$$

Since $\mathcal{B}^{(j)}$ are degree $(j-1)$ homogeneous functions (in cartesian coordinates) and the ϕ_n's decay exponentially in the sense of (2.28), there exists $K_n \in \mathbb{R}_+$ and $\epsilon_n > 0$ such that for all $0 < \epsilon \leq \epsilon_n$,

$$\left\| (H_0 + \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)})(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) - (\lambda_0 - \sum_{k=3}^{n} C_k \epsilon^k)(\phi_0 + \sum_{k=3}^{n} \epsilon^k \phi_k) \right\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq K_n \epsilon^{n+1}. \tag{4.21}$$

It remains to bound $\|(V_\epsilon - \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)})\psi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}$. From (2.6), (2.28) and (4.16), there exists $\epsilon_n > 0$, $\alpha_n > 0$ and $M_n \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$

$$\|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} \leq M_n.$$

Introducing

$$\Omega_\epsilon = \left\{(\mathbf{r}_1, \mathbf{r}_2) \in \mathbb{R}^3 \times \mathbb{R}^3 \; : \; |\mathbf{r}_1| + |\mathbf{r}_2| < (2\epsilon)^{-1}\right\}, \tag{4.22}$$

and the potentials defined by

$$\begin{aligned} v_\epsilon^{(1)}(\mathbf{r}_1, \mathbf{r}_2) &:= |\mathbf{r}_1 - \epsilon^{-1}\mathbf{e}|^{-1}, \\ v_\epsilon^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &:= |\mathbf{r}_2 + \epsilon^{-1}\mathbf{e}|^{-1}, \\ v_\epsilon^{(3)}(\mathbf{r}_1, \mathbf{r}_2) &:= |\mathbf{r}_1 - \mathbf{r}_2 - \epsilon^{-1}\mathbf{e}|^{-1}, \end{aligned} \tag{4.23}$$

we have,

$$\begin{aligned} \|(V_\epsilon - \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)})\phi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} &\leq \|(V_\epsilon - \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)})\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon)} \\ &+ \sum_{k=3}^{n} \epsilon^k \|\mathcal{B}^{(k)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} + \sum_{j=1}^{3} \|v_\epsilon^{(j)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} + \epsilon\|\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)}. \end{aligned}$$

We first see that

$$\|\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} \leq e^{-\alpha_n(2\epsilon)^{-1}}\|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} \leq M_n e^{-\alpha_n(2\epsilon)^{-1}}.$$

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

$$\begin{aligned} \sum_{k=3}^{n} \epsilon^k \|\mathcal{B}^{(k)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} &\leq \sum_{k=3}^{n} \epsilon^k \|\mathcal{B}^{(k)} e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\|_{L^\infty(\Omega_\epsilon^c)} \|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} \\ &\leq M_n \sum_{k=3}^{n} \epsilon^k \|\mathcal{B}^{(k)} e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\|_{L^\infty(\Omega_\epsilon^c)} \leq B_n \epsilon^3 e^{-\alpha_n(2\epsilon)^{-1}}. \end{aligned}$$

In addition, we have

$$\begin{aligned} \sum_{j=1}^{3} \|v_\epsilon^{(j)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} &\leq \sum_{j=1}^{3} e^{-\alpha_n(2\epsilon)^{-1}} \|v_\epsilon^{(j)} e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon^c)} \\ &\leq \sum_{j=1}^{3} e^{-\alpha_n(2\epsilon)^{-1}} \|v_\epsilon^{(j)} e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \\ &\leq 8e^{-\alpha_n(2\epsilon)^{-1}} \|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)} = 8e^{-\alpha_n(2\epsilon)^{-1}} M_n, \end{aligned}$$

where we have used the Hardy inequality in dimension 3

$$\forall \phi \in H^1(\mathbb{R}^3), \qquad \int_{\mathbb{R}^3} \frac{|\phi(\mathbf{r})|^2}{|\mathbf{r}|^2}\, d\mathbf{r} \le 4 \int_{\mathbb{R}^3} |\nabla \phi(\mathbf{r})|^2\, d\mathbf{r}$$

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

$$\begin{aligned} \|v_\epsilon^{(j)}\psi\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} &= \int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3} \frac{|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2}{|\mathbf{r}_j + (-1)^j\epsilon^{-1}\mathbf{e}|^2}\, d\mathbf{r}_j\right) d\mathbf{r}_{3-j} \\ &\le \int_{\mathbb{R}^3} 4\left(\int_{\mathbb{R}^3} |\nabla_{\mathbf{r}_j}\psi(\mathbf{r}_1,\mathbf{r}_2)|^2\, d\mathbf{r}_j\right) d\mathbf{r}_{3-j} \le 4\|\nabla_{\mathbf{r}_j}\psi\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}, \end{aligned}$$

for $j = 1, 2$, and

$$\begin{aligned} \|v_\epsilon^{(3)}\psi\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2 - \epsilon^{-1}\mathbf{e}|^2}\, d\mathbf{r}_1\, d\mathbf{r}_2 \\ &= \frac{1}{8}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\psi(\mathbf{r}_1' + \mathbf{r}_2', \mathbf{r}_1' - \mathbf{r}_2')|^2}{|\mathbf{r}_2' - \epsilon^{-1}\mathbf{e}|^2}\, d\mathbf{r}_1'\, d\mathbf{r}_2' \\ &\le \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} |(\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}_2})\psi(\mathbf{r}_1' + \mathbf{r}_2', \mathbf{r}_1' - \mathbf{r}_2')|^2\, d\mathbf{r}_1'\, d\mathbf{r}_2' \\ &= 4\|(\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}_2})\psi\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} = 8\|\nabla\psi\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}. \end{aligned}$$

From the multipolar expansion of V_ϵ, we know that there exist $c_n \in \mathbb{R}_+$

$$\left| V_\epsilon(\mathbf{r}_1,\mathbf{r}_2) - \sum_{i=3}^{n} \epsilon^i \mathcal{B}^{(i)}(\mathbf{r}_1,\mathbf{r}_2)\right| \le c_n K^n \epsilon^{n+1}, \quad \text{whenever } |\mathbf{r}_1| + |\mathbf{r}_2| \le K \le (2\epsilon)^{-1}. \tag{4.24}$$

Let us now show that (4.24) implies that there exists $\widetilde{c}_n \in \mathbb{R}_+$ such that for all $0 \le K \le (2\epsilon)^{-1}$,

$$\sup_{|\mathbf{r}_1|+|\mathbf{r}_2|\le K} \left| V_\epsilon(\mathbf{r}_1,\mathbf{r}_2) - \sum_{i=3}^{n} \epsilon^i \mathcal{B}^{(i)}(\mathbf{r}_1,\mathbf{r}_2)\right| e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)} \le \widetilde{c}_n \epsilon^{n+1}. \tag{4.25}$$

This is immediate from (4.24) for $K \le 1$, taking $\widetilde{c}_n = c_n$. Now we let $K > 1$. Then (4.24) implies

$$\sup_{(K/2)\le(|\mathbf{r}_1|+|\mathbf{r}_2|)\le K} \left| V_\epsilon(\mathbf{r}_1,\mathbf{r}_2) - \sum_{i=3}^{n} \epsilon^i \mathcal{B}^{(i)}(\mathbf{r}_1,\mathbf{r}_2)\right| e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)} \le c_n e^{-\alpha_n K/2} K^n \epsilon^{n+1}.$$

Applying this repeatedly for $2^{-j}K$ replacing K until $2^{-j}K < 1$ yields (4.25), with

$$\widetilde{c}_n = c_n \sup_{t\ge 0} t^n e^{-\alpha_n t/2}.$$

Applying (4.25) for $K = (2\epsilon)^{-1}$ yields

$$\|(V_\epsilon - \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)}) e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\|_{L^\infty(\Omega_\epsilon)} \le \widetilde{c}_n \epsilon^{n+1},$$

from which we obtain

$$\begin{aligned}&\|(V_\epsilon - \sum_{k=3}^n \epsilon^k \mathcal{B}^{(k)})\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon)}\\ \leq& \|(V_\epsilon - \sum_{k=3}^n \epsilon^k \mathcal{B}^{(k)})e^{-\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\|_{L^\infty(\Omega_\epsilon)}\|e^{\alpha_n(|\mathbf{r}_1|+|\mathbf{r}_2|)}\phi_\epsilon^{(n)}\|_{L^2(\Omega_\epsilon)}\\ \leq& \widetilde{c}_n M_n \epsilon^{n+1}.\end{aligned}$$

Finally, we get

$$\|(V_\epsilon - \sum_{k=3}^n \epsilon^k \mathcal{B}^{(k)})\phi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq \widetilde{c}_n M_n \epsilon^{n+1} + (8+\epsilon+B_n\epsilon^3)M_n e^{-\alpha_n(2\epsilon)^{-1}}. \quad (4.26)$$

Together with (4.21), this proves that there exists $c_n'' \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$,

$$\|r_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} = \|H_\epsilon \psi_\epsilon^{(n)} - \mu_\epsilon^{(n)}\psi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq c_n''\epsilon^{n+1}. \quad (4.27)$$

It follows from (4.18)-(4.19) that for $n \geq 3$ fixed, there exists $C \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$,

$$|\lambda_\epsilon - \mu_\epsilon^{(n)}| \leq C\epsilon^{2(n+1)} \quad \text{and} \quad \|\psi_\epsilon - \psi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \leq C\epsilon^{n+1}. \quad (4.28)$$

Then,

$$\begin{aligned}&\mu_\epsilon^{(n)} - \lambda_\epsilon^{(n)}\\ =&\langle \psi_\epsilon^{(n)}, H_\epsilon\psi_\epsilon^{(n)} - \lambda_\epsilon^{(n)}\psi_\epsilon^{(n)}\rangle\\ =&m_\epsilon^{(n)}\left\langle \psi_\epsilon^{(n)}, \mathcal{T}_\epsilon\Big[(V_\epsilon - \sum_{k=3}^n \epsilon^k\mathcal{B}^{(k)})\phi_\epsilon^{(n)} + \epsilon^n\sum_{k=1}^n \epsilon^k\Big(\sum_{j=k}^n \mathcal{B}^{(j)}\phi_{n+k-j} + \sum_{j=k}^n C_j\phi_{n+k-j}\Big)\Big]\right\rangle\end{aligned}$$

so that there exists a constant c_n such that for $0 < \epsilon \leq \epsilon_n$,

$$\begin{aligned}&\left|\mu_\epsilon^{(n)} - \lambda_\epsilon^{(n)}\right|\\ \leq& 2\left\|(V_\epsilon - \sum_{k=3}^n \epsilon^k\mathcal{B}^{(k)})\phi_\epsilon^{(n)} + \epsilon^n\sum_{k=1}^n \epsilon^k\Big(\sum_{j=k}^n \mathcal{B}^{(j)}\phi_{n+k-j} + \sum_{j=k}^n C_j\phi_{n+k-j}\Big)\right\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}\\ \leq& c_n\epsilon^{n+1}.\end{aligned}$$

The error bounds on the eigenvalue errors in (2.12) follow from (4.28) and the above inequality.

Finally, the error $\xi_\epsilon^{(n)} = \psi_\epsilon - \psi_\epsilon^{(n)}$, as defined in [13], satisfies

$$H_\epsilon\xi_\epsilon^{(n)} = \lambda_\epsilon\psi_\epsilon - H_\epsilon\psi_\epsilon^{(n)} = \lambda_\epsilon - \mu_\epsilon^{(n)} - r_\epsilon^{(n)} =: \eta_\epsilon^{(n)}.$$

From (4.27)-(4.28), there exists a constant $c_n \in \mathbb{R}_+$ such that for all $0 < \epsilon \leq \epsilon_n$,

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

In addition,

$$-\frac{1}{2}\Delta\xi_\epsilon^{(n)} = -W_\epsilon\xi_\epsilon^{(n)} + \eta_\epsilon^{(n)}, \quad (4.29)$$

where

$$W_\epsilon(\mathbf{r}_1,\mathbf{r}_2) := -\frac{1}{|\mathbf{r}_1-(2\epsilon)^{-1}\mathbf{e}|}-\frac{1}{|\mathbf{r}_2-(2\epsilon)^{-1}\mathbf{e}|}-\frac{1}{|\mathbf{r}_1+(2\epsilon)^{-1}\mathbf{e}|}-\frac{1}{|\mathbf{r}_2+(2\epsilon)^{-1}\mathbf{e}|}+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\epsilon.$$

Proceeding as in [13, Section 2.4], we use the Hardy inequality in $\mathbb{R}^3$ and the Cauchy-Schwarz inequality to obtain that

$$\begin{aligned}&\frac{1}{2}\|\nabla\xi_\epsilon^{(n)}\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} = \langle \xi_\epsilon^{(n)}, -W_\epsilon\xi_\epsilon^{(n)}+\eta_\epsilon^{(n)}\rangle\\ \leq&(10\|\nabla\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}+\epsilon\|\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}+\|\eta_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)})\|\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)},\\ &\frac{1}{2}\|\Delta\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} = \|-W_\epsilon\xi_\epsilon^{(n)}+\eta_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}\\ \leq&10\|\nabla\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}+\epsilon\|\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}+\|\eta_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}.\end{aligned}$$

It follows from (4.29) that there exists a constant $c_n\in\mathbb{R}_+$ such that for all $0<\epsilon\leq\epsilon_n$, $\|\Delta\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}\leq c_n\epsilon^{n+1}$, and thus $\|\xi_\epsilon^{(n)}\|_{H^2(\mathbb{R}^3\times\mathbb{R}^3)}\leq c_n\epsilon^{n+1}$.

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Appendix A.

A.1. Multipolar expansion of V_ϵ. We start from the well-known multipolar expansion of $\frac{1}{|\mathbf{r}-R\mathbf{e}|}$ in terms of Legendre polynomials

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

a straightforward consequence of the definition of Legendre polynomials via their generating function [38]

$$\forall -1\leq x\leq 1,\quad \left(1-2xt+t^2\right)^{-1/2}=\sum_{k=0}^{\infty}P_k(x)t^k, \tag{A.2}$$

taking

$$-1\leq x=\frac{\mathbf{r}\cdot\mathbf{e}}{|\mathbf{r}|}\leq 1,\qquad t=\frac{|\mathbf{r}|}{R}.$$

Since the Legendre polynomials are at most 1 in magnitude on the interval $[-1,1]$, the sum in (A.2) converges absolutely for all $|t|<1$, and

$$\left|\sum_{k=n}^{\infty}P_k(x)t^k\right|\leq\sum_{k=n}^{\infty}t^k=\frac{t^n}{1-t}\leq 2t^n,\quad \text{for all } |t|\leq\tfrac{1}{2}.$$

Consequently,

$$\left| \frac{1}{|\mathbf{r} - R\mathbf{e}|} - \frac{1}{R} \left(\sum_{k=0}^{n-1} P_k \left(\frac{\mathbf{r} \cdot \mathbf{e}}{|\mathbf{r}|} \right) \left(\frac{|\mathbf{r}|}{R} \right)^k \right) \right| \leq 2 \frac{|\mathbf{r}|^n}{R^{n+1}}, \quad \text{for all } |\mathbf{r}| \leq R/2. \tag{A.3}$$

Recalling that $P_0(x) = 1$, $P_1(x) = x$ and

$$V_\epsilon(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 - \epsilon^{-1}\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \epsilon^{-1}\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \epsilon^{-1}\mathbf{e}|} + \epsilon,$$

with $\epsilon = R^{-1}$, we deduce from (A.3) that

$$\left| V_\epsilon(\mathbf{r}_1, \mathbf{r}_2) - \sum_{k=3}^{n} \epsilon^k \mathcal{B}^{(k)}(\mathbf{r}_1, \mathbf{r}_2) \right| \leq 6K^n \epsilon^{n+1}, \quad \text{whenever } |\mathbf{r}_1| + |\mathbf{r}_2| \leq K \leq (2\epsilon)^{-1}, \tag{A.4}$$

where the polynomial functions $\mathcal{B}^{(k)}$ are given by

$$\begin{aligned} \mathcal{B}^{(k)}(\mathbf{r}_1, \mathbf{r}_2) :=& P_{k-1} \left(\frac{(\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{e}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) |\mathbf{r}_1 - \mathbf{r}_2|^{k-1} - P_{k-1} \left(\frac{\mathbf{r}_1 \cdot \mathbf{e}}{|\mathbf{r}_1|} \right) |\mathbf{r}_1|^{k-1} \\ & - P_{k-1} \left(-\frac{\mathbf{r}_2 \cdot \mathbf{e}}{|\mathbf{r}_2|} \right) |\mathbf{r}_2|^{k-1}. \end{aligned}$$

This proves (4.24). To derive the expression (2.14) for the $\mathcal{B}^{(k)}$'s, we first use the identities

$$P_l(\sigma \cdot \sigma') = \left(\frac{4\pi}{2l+1} \right) \sum_{m=-l}^{l} (-1)^m Y_l^m(\sigma) Y_l^m(\sigma'), \qquad \sqrt{\frac{4\pi}{2l+1}} Y_l^m(\mathbf{e}) = \delta_{m,0},$$

valid for all $l \in \mathbb{N}$, $-l \leq m \leq l$, $\sigma, \sigma' \in \mathbb{S}^2$ (recall that $\mathbf{e}$ is the unit vector of the z-axis), and get

$$\begin{aligned} \mathcal{B}^{(k)}(\mathbf{r}_1, \mathbf{r}_2) :=& \sqrt{\frac{4\pi}{2k-1}} \Bigg(Y_{k-1}^0 \left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) |\mathbf{r}_1 - \mathbf{r}_2|^{k-1} \\ & - Y_{k-1}^0 \left(\frac{\mathbf{r}_1}{|\mathbf{r}_1|} \right) |\mathbf{r}_1|^{k-1} - Y_{k-1}^0 \left(-\frac{\mathbf{r}_2}{|\mathbf{r}_2|} \right) |\mathbf{r}_2|^{k-1} \Bigg). \end{aligned}$$

We next use the addition formula [36] stating that for $l \in \mathbb{N}$, $\mathbf{r}_1, \mathbf{r}_2 \in \mathbb{R}^3$,

$$\begin{aligned} & \sqrt{\frac{4\pi}{2l+1}} Y_l^0 \left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) |\mathbf{r}_1 - \mathbf{r}_2|^l \\ &= \sum_{l_1 + l_2 = l} \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} G_c(l_1, l_2, m) r_1^{l_1} Y_{l_1}^m \left(\frac{\mathbf{r}_1}{|\mathbf{r}_1|} \right) r_2^{l_2} Y_{l_2}^{-m} \left(\frac{\mathbf{r}_2}{|\mathbf{r}_2|} \right), \end{aligned}$$

where

$$\begin{aligned} G_c(l_1, l_2, m) &= (-1)^{l_2} \frac{4\pi}{((2l_1+1)(2l_2+1))^{1/2}} \binom{l_1 + l_2}{l_1 + m}^{1/2} \binom{l_1 + l_2}{l_1 - m}^{1/2}, \\ &= (-1)^{l_2} \frac{4\pi (l_1 + l_2)!}{((2l_1+1)(2l_2+1)(l_1+m)!(l_2+m)!(l_1-m)!(l_2-m)!)^{1/2}}. \end{aligned}$$

As for $G_c(l,0,0) = G_c(0,l,0) = \frac{4\pi}{(2l+1)^{1/2}}$ and $Y_0^0 = \frac{1}{\sqrt{4\pi}}$, we finally obtain (2.14).

Appendix B. Wigner $(2n+1)$ **rule.** Using the notation in (4.16), we consider the Rayleigh quotients

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

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

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

We deduce from the boundedness of the ϕ_n's in $H^2(\mathbb{R}^3 \times \mathbb{R}^3)$, the Hardy inequality in $\mathbb{R}^3$, and the estimates (2.28) and (4.24), that there exist $C \in \mathbb{R}_+$, $\beta_n > 0$ and $\epsilon_n > 0$ such that for all $0 \le \epsilon \le \epsilon_n$

$$\|\phi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \le 2, \qquad \|\eta_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \le C,$$
$$\|\upsilon_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \le C\epsilon^{2n+2}, \qquad \|\xi_\epsilon^{(n)}\|_{L^2(\mathbb{R}^3\times\mathbb{R}^3)} \le Ce^{-\beta_n \epsilon},$$

proceeding as in the proof of (4.26) to establish the third inequality. It follows from (2.12) and the above bounds that

$$\begin{aligned}
\widetilde{\mu}_\epsilon^{(n)} &= \lambda_\epsilon + \widetilde{\mu}_\epsilon^{(n)} - \mu_\epsilon^{(n)} + O(\epsilon^{2n+2}) \\
&= \lambda_\epsilon + \frac{\left\langle \phi_\epsilon^{(n)}, \left(H_0 + \sum_{i=3}^{2n+1} \epsilon^i \mathcal{B}^{(i)} \right) \phi_\epsilon^{(n)} \right\rangle}{\|\phi_\epsilon^{(n)}\|^2_{L^2(\mathbb{R}^3\times\mathbb{R}^3)}} - \frac{\left\langle \mathcal{T}_\epsilon^* \mathcal{T}_\epsilon \phi_\epsilon^{(n)}, (H_0 + V_\epsilon)\phi_\epsilon^{(n)} \right\rangle}{\left\langle \mathcal{T}_\epsilon^* \mathcal{T}_\epsilon \phi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \right\rangle} + O(\epsilon^{2n+2}) \\
&= \lambda_\epsilon - \frac{\left\langle \phi_\epsilon^{(n)}, \upsilon_\epsilon^{(n)} \right\rangle}{\left\langle \phi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \right\rangle} + \frac{\left\langle \xi_\epsilon^{(n)}, \eta_\epsilon^{(n)} \right\rangle - \left\langle \xi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \right\rangle \left\langle \phi_\epsilon^{(n)}, \eta_\epsilon^{(n)} \right\rangle}{\left\langle \phi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \right\rangle + \left\langle \xi_\epsilon^{(n)}, \phi_\epsilon^{(n)} \right\rangle} + O(\epsilon^{2n+2}) \\
&= \lambda_\epsilon + O(\epsilon^{2n+2}) = -1 - \sum_{k=6}^{2n+1} C_k \epsilon^k + O(\epsilon^{2n+2}).
\end{aligned}$$

Thus, the coefficients C_k for $k \le 2n+1$ can be computed from the Taylor expansion of $\widetilde{\mu}_\epsilon^{(n)}$ up to order $(2n+1)$, which only involves the ϕ_k's for $k \le n$, and the $\mathcal{B}^{(k)}$'s for $k \le (2n+1)$. To obtain a computable expression of the coefficients C_{2n} and C_{2n+1}, we first use Equation (2.9), which can be rewritten as

$$H_0 \phi_k + \sum_{j=3}^{k} \mathcal{B}^{(j)} \phi_{k-j} = -C_0 \phi_k - \sum_{j=6}^{k} C_j \phi_{k-j} = -\sum_{j=0}^{k} C_j \phi_{k-j}, \tag{B.1}$$

with $C_0 = 1$ and $C_i = 0$ for $i = 1, ..., 5$, to get that for all $n \ge 1$

$$\begin{aligned}
\nu_\epsilon^{(n)} &:= \left\langle \phi_\epsilon^{(n)}, \left(H_0 + \sum_{i=3}^{2n+1} \epsilon^i \mathcal{B}^{(i)} \right) \phi_\epsilon^{(n)} \right\rangle \\
&= -\sum_{l=0}^{n} \epsilon^l \sum_{i=0}^{l} \left\langle \phi_i, \sum_{j=0}^{l-i} C_j \phi_{l-i-j} \right\rangle
\end{aligned}$$

$$+\,\epsilon^n \sum_{l=1}^{n} \epsilon^l \left(-\sum_{i=l}^{n} \left\langle \phi_i, \sum_{j=0}^{n+l-i} C_j \phi_{n+l-i-j} \right\rangle + \sum_{i=0}^{l-1} \left\langle \phi_i, \sum_{j=0}^{n} \mathcal{B}^{(n+l-i-j)} \phi_j \right\rangle \right)$$
$$+\,\epsilon^{2n+1} \sum_{i=0}^{n} \left\langle \phi_i, \sum_{j=0}^{n} \mathcal{B}^{(2n+1-i-j)} \phi_j \right\rangle + O(\epsilon^{2n+2}). \tag{B.2}$$

In addition, we have

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

and, using the relation $\sum_{i=0}^{k} \left\langle \phi_i, \phi_{k-i} \right\rangle = 0$ derived from (2.10), we get

$$\|\phi_\epsilon^{(n)}\|^2 = 1 + \epsilon^n \sum_{k=1}^{n} \epsilon^k \sum_{i=k}^{n} \left\langle \phi_i, \phi_{n+k-i} \right\rangle. \tag{B.3}$$

It follows from (B.2)-(B.3) that

$$\widetilde{\mu}_\epsilon^{(n)} = \frac{\nu_\epsilon^{(n)}}{\|\phi_\epsilon^{(n)}\|^2} = -\sum_{k=0}^{2n+1} C_k \epsilon^k + O(\epsilon^{2n+2}),$$

with

$$\begin{aligned} C_{2n} =& \left\langle \phi_n, \sum_{j=0}^{n} C_j \phi_{n-j} \right\rangle - \sum_{i=0}^{n-1} \left\langle \phi_i, \sum_{j=0}^{n} \mathcal{B}^{(2n-i-j)} \phi_j \right\rangle \\ & - \sum_{k=1}^{n} \left(\sum_{i=k}^{n} \left\langle \phi_i, \phi_{n+k-i} \right\rangle \right) \sum_{i=0}^{n-k} \left\langle \phi_i, \sum_{j=0}^{n-k-i} C_j \phi_{n-k-i-j} \right\rangle, \end{aligned}$$

and

$$\begin{aligned} C_{2n+1} =& -\sum_{i=0}^{n} \left\langle \phi_i, \sum_{j=0}^{n} \mathcal{B}^{(2n+1-i-j)} \phi_j \right\rangle \\ & - \sum_{k=1}^{n} \left(\sum_{i=k}^{n} \left\langle \phi_i, \phi_{n+k-i} \right\rangle \right) \sum_{i=0}^{n+1-k} \left\langle \phi_i, \sum_{j=0}^{n+1-k-i} C_j \phi_{n+1-k-i-j} \right\rangle. \end{aligned}$$

Appendix C. Computation of the integrals S_n in (3.6).

Recall that

$$S_n = \int_0^{+\infty} r^3 e^{-r} \varphi_{n,1}(r) \mathrm{d}r,$$

where

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

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 $k, k', m \in \mathbb{N}$,

$$\int_0^\infty x^m L_k^{(m)}(x) L_{k'}^{(m)}(x) e^{-x} \,\mathrm{d}x = \frac{(k+m)!}{k!}\delta_{k,k'}; \tag{C.1}$$

- for all $\gamma \in \mathbb{C}$ such that $\Re(\gamma) > -\frac{1}{2}$, and $m \in \mathbb{N}$,

$$e^{-\gamma x} = \sum_{k=0}^{+\infty} \frac{\gamma^k}{(1+\gamma)^{k+m+1}} L_k^{(m)}(x); \tag{C.2}$$

- for all $k, m \in \mathbb{N}$,

$$x L_k^{(m+1)}(x) = (k+m+1) L_k^{(m)}(x) - (k+1) L_{k+1}^{(m)}(x). \tag{C.3}$$

By a change of variable, we obtain

$$S_n = \frac{n^2}{8}\sqrt{\frac{(n-2)!}{(n+1)!}} I_n \quad \text{with} \quad I_n := \int_0^{+\infty} x^4 L_{n-2}^{(3)} e^{-\frac{n-1}{2}x} e^{-x}\,dx.$$

Applying (C.2) for $\gamma = \frac{n-1}{2}$ and $m = 4$, then (C.3) for $m = 3$, and finally (C.1) for $m = 3$, we obtain

$$\begin{aligned}
I_n &= \int_0^{+\infty} x^4 L_{n-2}^{(3)} \left(\sum_{k=0}^{+\infty} \frac{2^5 (n-1)^k}{(n+1)^{k+5}} L_k^{(4)}(x) \right) e^{-x}\,dx \\
&= \int_0^{+\infty} x^3 L_{n-2}^{(3)} \left(\sum_{k=0}^{+\infty} \frac{2^5 (n-1)^k}{(n+1)^{k+5}} \left((k+4) L_k^{(3)}(x) - (k+1) L_{k+1}^{(3)}(x) \right) \right) e^{-x}\,dx \\
&= \sum_{k=0}^{+\infty} \frac{2^5 (n-1)^k}{(n+1)^{k+5}} \left((k+4)\frac{(k+3)!}{k!}\delta_{k,n-2} - (k+1)\frac{(k+4)!}{(k+1)!}\delta_{k+1,n-2} \right) \\
&= \frac{2^5 (n-1)^{n-2}}{(n+1)^{n+3}} (n+2) \frac{(n+1)!}{(n-2)!} - \frac{2^5 (n-1)^{n-3}}{(n+1)^{n+2}} (n-2) \frac{(n+1)!}{(n-2)!} \\
&= \frac{2^6 n (n-1)^{n-3}}{(n+1)^{n+3}} \frac{(n+1)!}{(n-2)!}.
\end{aligned}$$

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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