Ground state energy of diatomic molecules in the Quantum Drude Oscillator model

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Abstract

TO DO

- Talk about the fact that the large coefficients c_n and d_n are polynomials in ϵ and S. In particular, it gives us access to only a finite number of energy levels. In particular c_n is of degree $(\lfloor n/2 \rfloor, 1)$ in (ϵ, S). Solving for S using one of the two equations and plugging back in the other, one gets a rational function of ϵ. The number of zeros is then bounded (some roots might be complex or there could be some simplifications between numerator and denominator) by the degree of the numerator.

INTRODUCTION

A Quantum Drude Oscillator (QDO) is a very simple atomistic model in which the properties of an atom are encompassed in a small number of parameters. The model consists in assimilating the atom to a point particle of mass m and electric charge $-q$ attached to a fixed (infinite mass) center of charge $+q$ by a harmonic spring characterized by a frequency ω. Molecules are then defined as a collections of QDOs interactig through Coulomb interactions.

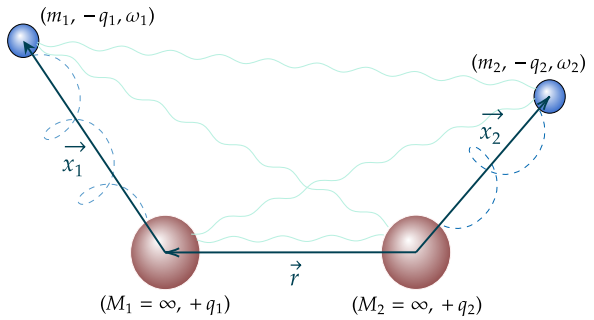

FIG. 1. Pair of interacting QDOs.

This simple model has been extensively used in various contexts, for instance in order to tackle the electronic structure problem for isolated molecules, in particular long range interactions, as well as to study the impact of an ambient bath or of an external electric field on molecular properties [1].

Even though the harmonic oscillator nature of the atomic constituents in this model drastically simplify the complexity of problem, the all-body Coulomb interaction remains challenging. One possible way to proceed is to treat the Coulomb interaction by performing a multipolar expansion.

By truncating the multipolar expansion up to Dipole-Dipole, one obtain a quadratic Hamiltonian, hence the quantum Hamiltonian can be analytically diagonalized. Though simple, this system was shown to capture long-range phenomena in large atomistic systems [2].

In the present work, we focus instead on small (diatomic) molecules in 1d, and treat in an *analytical* way the Coulombic interactions up to Quadrupole-Quadrupole and Dipole-Octupole order, paving the way towards generalization for larger systems.

GitHub repository: The reader will find an open source code accompanying this paper following this link.

QUARTIC HAMILTONIAN FOR DIATOMIC MOLECULES

Multipolar expansion for the Coulomb potential

The Hamiltonian describing a system of N QDOs in 3d is given by:

$$H = \sum_{i=1}^{N} \left[\frac{1}{2} m_i \dot{\vec{x}}_i^2 + \frac{1}{2} m_i \omega_i^2 \vec{x}_i^2 \right] + \sum_{i<j} V_{\text{Coul}}\left(\vec{x}_i, \vec{x}_j\right) , \quad (1)$$

with the Coulomb interaction given by

$$\frac{V_{\text{Coul}}\left(\vec{x}_1, \vec{x}_2\right)}{q_1 q_2 (4\pi\epsilon_0)^{-1}} = \frac{1}{r} - \frac{1}{|\vec{r} + \vec{x}_1|} - \frac{1}{|\vec{r} - \vec{x}_2|} + \frac{1}{|\vec{r} - \vec{x}_2 + \vec{x}_1|}$$

In the multipolar expansion, this can be expressed as:

$$V_{\text{Coul}}\left(\vec{x}_1, \vec{x}_2\right) = \sum_{n \geq 0} V_n\left(\vec{x}_1, \vec{x}_2\right) , \quad (2)$$

with the following scaling behavior in terms of the distance between the centers:

$$V_n\left(\vec{x}_1, \vec{x}_2\right) \propto r^{-n+3} . \quad (3)$$

The first terms in that multipolar expansion have the following interpretation:

- $n = 0$: Dipole-Dipole interaction (DD),
- $n = 1$: Dipole-Quadrupole interaction (DQ),
- $n = 2$: Quadrupole-Quadrupole and Dipole-Octupole interaction (QQ+DO).

Using the following identity for generic vectors $\vec{r}$ and $\vec{\epsilon}$:

$$\frac{1}{|\vec{r}-\vec{\epsilon}|} = \frac{1}{r}\left[1 + \frac{\vec{\epsilon}\cdot\hat{r}}{r} - \frac{\epsilon^2 - 3(\vec{\epsilon}\cdot\hat{r})^2}{2r^2} + \frac{5(\vec{\epsilon}\cdot\hat{r})^3 - 3\epsilon^2(\vec{\epsilon}\cdot\hat{r})}{2r^3} + \frac{35(\vec{\epsilon}\cdot\hat{r})^4 - 30\epsilon^2(\vec{\epsilon}\cdot\hat{r})^2 + 3\epsilon^4}{8r^4} + \mathcal{O}\left(\frac{\epsilon^5}{r^5}\right)\right] \tag{4}$$

one can explicitely compute V_0, V_1 and V_2. Instead of writting out the expression of these potentials in full glory, let us now restrict ourselves to a system composed of $N = 2$ QDOs.

Reduced particle system

Let us move to the center of mass frame, in which the dynamics reduces to that of an effective reduced particle:

$$\vec{x} := \vec{x}_1 - \vec{x}_2 \tag{5a}$$
$$m_1\vec{x}_1 + m_2\vec{x}_2 = \vec{0}\,. \tag{5b}$$

In terms of the reduced variable, a straightforward computation gives us:

$$V_0(\vec{x}) = -\frac{m_1m_2}{(m_1+m_2)^2}\cdot\frac{x^2 - 3(\vec{x}\cdot\hat{r})^2}{4\pi\epsilon_0 r^3}\,, \tag{6a}$$
$$V_1(\vec{x}) = \frac{3m_1m_2}{2(m_1+m_2)^2}\cdot\frac{(\vec{x}\cdot\hat{r})\left(3x^2 - 5(\vec{x}\cdot\hat{r})^2\right)}{4\pi\epsilon_0 r^4}\,, \tag{6b}$$
$$V_2(\vec{x}) = \frac{m_1m_2(2m_1^2+3m_1m_2+2m_2^2)}{4(m_1+m_2)^4}\times \tag{6c}$$
$$\times\,\frac{3x^4 - 30(\vec{x}\cdot\hat{r})^2x^2 + 35(\vec{x}\cdot\hat{r})^4}{4\pi\epsilon_0 r^5}\,.$$

Let us now assume that the system is effectively one-dimensional, aligned along the direction on which the centers of the two QDOs are sitting. One obtain the following one-dimensional potentials for an effective particle of mass $m_1m_2/(m_1+m_2)$:

$$V_0(x) = \frac{2m_1m_2}{(m_1+m_2)^2}\cdot\frac{2x^2}{4\pi\epsilon_0 r^3}\,, \tag{7a}$$
$$V_1(x) = -\frac{3m_1m_2}{(m_1+m_2)^2}\cdot\frac{\mathrm{sgn}(\vec{x}\cdot\hat{r})|x|x^2}{4\pi\epsilon_0 r^4} = -\frac{3m_1m_2}{(m_1+m_2)^2}\cdot\frac{x^3}{4\pi\epsilon_0 r^4}\,, \tag{7b}$$
$$V_2(x) = \frac{2m_1m_2(2m_1^2+3m_1m_2+2m_2^2)}{(m_1+m_2)^4}\cdot\frac{x^4}{4\pi\epsilon_0 r^5}\,. \tag{7c}$$

As a comment concerning this possible sign issue: maybe one can argue that provided the external field is strong enough, we can take x^3.

Including the contribution of the harmonic potentials present in (1) and coupling the system to an external electric field, one finally obtain the following total one-dimensional potential:

$$V(x) = \alpha x + \beta x^2 + \gamma x^3 + \delta x^4\,, \tag{8}$$

with the following expression of the coupling constants:

$$\alpha = -\frac{m_1q_2 + m_2q_1}{m_1+m_2}\cdot\mathcal{E} \tag{9a}$$
$$\beta = \frac{m_1m_2}{(m_1+m_2)^2}\cdot\frac{2q_1q_2}{4\pi\epsilon_0 r^3} + \frac{1}{2}\cdot\frac{m_1m_2}{m_1+m_2}\cdot\frac{m_1\omega_2^2 + m_2\omega_1^2}{m_1+m_2} \tag{9b}$$
$$\gamma = -\frac{m_1m_2}{(m_1+m_2)^2}\cdot\frac{3q_1q_2}{4\pi\epsilon_0 r^4}\,, \tag{9c}$$
$$\delta = \frac{2m_1m_2(2m_1^2+3m_1m_2+2m_2^2)}{(m_1+m_2)^4}\cdot\frac{q_1q_2}{4\pi\epsilon_0 r^5}\,. \tag{9d}$$

ANALYTIC SOLUTION OF THE SCHRÖDINGER EQUATION

In what follows, we define $k^2 := \frac{m_1+m_2}{m_1m_2}\frac{\hbar^2}{2}$. Let us consider the time-independent Schrödinger equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{\epsilon - V(x)}{k^2}\right]\psi(x) = 0\,, \tag{10}$$

where the potential V is provided by (8) and (9). Performing the following change of variable:

$$\psi(x) = \exp\left[\frac{\gamma^2 - 4\beta\delta}{8k\delta^{3/2}}\,x - \frac{\gamma}{4k\delta^{1/2}}\,x^2 - \frac{\delta^{1/2}}{3k}\,x^3\right]\phi(x) \tag{11}$$

we obtain:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}(x) + \left[\frac{\gamma^2 - 4\beta\delta}{4k\delta^{3/2}} - \frac{\gamma}{k\delta^{1/2}}\,x - \frac{2\delta^{1/2}}{k}\,x^2\right]\frac{\mathrm{d}\phi}{\mathrm{d}x}(x) + \left[\frac{16\delta^2\left(\beta^2 + 4\delta\epsilon\right) - 8\beta\gamma^2\delta + \gamma^4 - 32\gamma\delta^{5/2}k}{64\delta^3k^2} - \frac{8\alpha\delta^2 - 4\beta\gamma\delta + \gamma^3 + 16\delta^{5/2}k}{8\delta^2k^2}\,x\right]\phi(x) = 0\,, \tag{12}$$

which is known as the so-called *tri-confluent Heun equation*. We further perform the following change of variable, the reason why to become clear soon:

$$\phi(x) = (1+x)^{\frac{4\beta\gamma\delta - \gamma^3 - 8\delta^2\left(\alpha + 2k\delta^{1/2}\right)}{16k\delta^{5/2}}} f(x)\,, \tag{13}$$

as well as map the positive real axis to the segment $[0,1]$ through the change of argument

$$z = \frac{x}{x+1}\,, \tag{14}$$

and look for a solution of the obtained ODE in terms of a series expansion at zero of the form:

$$f(z) = \sum_{n\geq 0} c_n z^n\,. \tag{15}$$

Plugging the ansatz into the differential equation, we obtain the following recurrence relation between the coefficients:

$$\begin{aligned}&(n+1)(n+2)c_{n+2} + (n+1)(A-4n)c_{n+1} + [6(n-1)n + Bn + E]c_n \\ &+ [C(n-1) + F - 4(n-2)(n-1)]c_{n-1} + [(n-3)(n-2) + D(n-2) + G]c_{n-2} = 0 \quad (n \geq 2)\end{aligned} \tag{16}$$

where the various coefficients are listed in full details in appendix. The coefficients c_0 and c_1 are to be fixed through boundary conditions, and the coeffients c_2 and c_3 are in turn fixed by the following relations

$$\begin{aligned}c_2 &= -Ec_0 - Ac_1\,,\\ c_3 &= -\frac{Fc_0 + (B+E)c_1 + 2(A-4)c_2}{6}\,.\end{aligned} \tag{17}$$

RESULTS

TABLE I. Ground state energy (in Ha) of the H-H system

r (a.u.) \ $\mathcal{E}$ (unit)	0.0	1.0	2.0
1.0	5.428021	1.000000	3.673658
2.0	0.531071	0.210137	0.872826
3.0	1.532129	0.957917	0.999836
4.0	1.968642	0.999963	1.000023
5.0	0.031075	1.000000	1.014180
6.0	0.978062	5.375749	0.970292
7.0	21.654276	0.558010	-34.785660
8.0	43.488829	85.452632	-28.868817

TABLE II. Ground state energy (in Ha) of the He-He system

r (a.u.) \ $\mathcal{E}$ (unit)	0.0	1.0	2.0
1.0	1.000000	1.000000	5.739538
2.0	1.266281	1.134311	-0.966946
3.0	0.880808	0.147328	-0.206244
4.0	3.755382	0.136923	1.000000
5.0	1.000000	0.999847	0.415453
6.0	6.604936	1.000000	-1.709232
7.0	1.000008	1.000000	9.223832
8.0	198.102785	1.000000	20.246740

Atomic data

We collect here the QDO parameters obtained in [3].

TABLE III. Parameters for QDOs (in a.u.)

	ω	m	q
H	0.4273	0.6099	0.7080
Li	0.0687	1.2545	0.9848
K	0.0630	0.8101	0.9670
Rb	0.0603	0.7343	0.9274
Cs	0.0531	0.6939	0.8950
He	1.0187	0.5083	0.8532
Ne	1.2965	0.3491	1.2494
Ar	0.7272	0.3020	1.3314
Kr	0.6359	0.2796	1.3741
Xe	0.5152	0.2541	1.3570

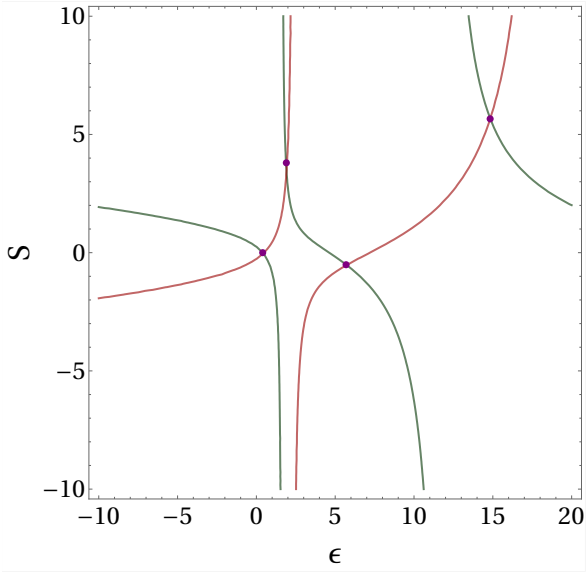

FIG. 2. Intersection loci of c_{20} and d_{20} with the $z = 0$ plane

Details on the derivation

$$A = -\frac{8\delta^2(\alpha+\beta) - 2\gamma\delta(2\beta+\gamma) + \gamma^3 + 32\delta^{5/2}k}{8\delta^{5/2}k}$$

$$B = \frac{8\delta^2(3\alpha+2\beta-\gamma) - 4\gamma\delta(3\beta+\gamma) + 3\gamma^3 + 96\delta^{5/2}k}{8\delta^{5/2}k}$$

$$C = -\frac{8\delta^2(3\alpha+\beta-\gamma) - 2\gamma\delta(6\beta+\gamma) + 3\gamma^3 + 16\delta^3 + 96\delta^{5/2}k}{8\delta^{5/2}k}$$

$$D = \frac{-4\beta\gamma\delta + \gamma^3 + 8\delta^2\left(\alpha + 4\sqrt{\delta}k\right)}{8\delta^{5/2}k}$$

$$E = \frac{4\gamma^2\delta^2\left(\gamma(4\alpha+\gamma) + 4\beta^2 + 8\beta\gamma\right) - 32\gamma\delta^3(\alpha+\beta)(2\beta+\gamma) + 64\delta^4(\alpha+\beta)^2 - 4\gamma^4\delta(2\beta+\gamma) + \gamma^6 + 256\delta^5\left(2k^2+\epsilon\right) + 128\delta^{9/2}k(3}{256\delta^5k^2}$$

$$F = -\frac{\left(-4\beta\gamma\delta + \gamma^3 + 8\delta^2\left(\alpha + 2\sqrt{\delta}k\right)\right)\left(-4\gamma\delta(\beta+2\delta) + \gamma^3 - 2\gamma^2\delta + 8\delta^2\left(\alpha+\beta+2\delta+4\sqrt{\delta}k\right)\right)}{128\delta^5k^2}$$

$$G = \frac{\left(-4\beta\gamma\delta + \gamma^3 + 8\delta^2\left(\alpha + 2\sqrt{\delta}k\right)\right)\left(-4\beta\gamma\delta + \gamma^3 + 8\delta^2\left(\alpha + 4\sqrt{\delta}k\right)\right)}{256\delta^5k^2}$$

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