He_2 molecule inside a prolate spheroidal box

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Plan

- Formalism: variational method & supersimmetry.
- Confined Helium atom in a spherical cavity.
  - Variational approach.
  - Trial eigenfunctions.
  - Results for ground state energies.
- Two helium atoms interacting within a prolate spheroidal box (ellipsoid).
  - Trial functions.
  - Variational energies eigenvalues.
- Results: He_2 ground state energies as a function of the distance between atomic nuclei.
- Conclusions.

Formalism

- Variational Method

$$\langle H \rangle = \frac{\int \psi_\gamma^{*}(r)\hat{H}\psi_\gamma(r)\,dr}{\int \left|\psi_\gamma(r)\right|^2 dr} \geq E$$

- $\psi_\gamma(r)$ → trial function
- γ → variational parameters
- Variational Principle: If an arbitrary function Ψ is used to compute the energy of a quantum system, the calculated value is always greater than or equal to the energy eigenvalue.

Formalism

- Supersymmetric Quantum Mechanics (SQM)
- First step => Ground state (E_0)
- Taking the Hamiltonian:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(r)}{dr^2}+V_{eff}(r)\psi(r)=E\psi(r)$$

- $V_{eff}(r)$ is the potential (including the barrier of potential in 3D problems).

Formalism

- Factorizing the Hamiltonian:

$$H - E_0 = \left(-\frac{d}{dr} + w(r)\right)\left(\frac{d}{dr} + w(r)\right)\psi(r) = 0$$

- *w(r)* is a function called superpotential.
- For simplicity: $\hbar^2 = 2m = 1$

- Using the Hamiltonian definition, we get:

$$w^2(r) - w'(r) = V_{eff}(r) - E$$

Ricatti equation

Formalism

- If we know the superpotential, we get:
- the ground state eigenvalue, E.
- the ground state eigenfunction:

$$\left(\frac{d}{dr}+w(r)\right)\psi(r)=0 \quad \rightarrow \quad \psi(r)\propto \exp\left(-\int w(r)\,dr\right)$$

Exact solution

- If it is not possible to obtain w from the Ricatti equation, it is possible to search an **approximate solution**, w_{ap} , for the superpotential.
- This solution w_{ap} generates a wave function that supplies an appropriate **trial function** for the Variational Method.

Formalism

The superpotential suggested* for the confined hydrogen atom is:

$$W(r) = -\frac{\mu_1}{r} + \frac{\mu_2}{R-r} + \mu_3$$

Trial function sugested* for hydrogen atom:

$$\Psi(\mu_1, \mu_2, \mu_3, r) \propto r^{\mu_1} \left(R-r\right)^{\mu_2} e^{-\mu_3 r}$$

*E. Drigo Filho and R. M. Ricotta, Phys. Lett. **A299** (2002) 137

He in a spherical cavity

- Trial function, inspired by the hydrogen atom results:

$$\psi \propto (r_1 r_2)^{\mu_2} e^{-\mu_1 (r_1 + r_2)} (r_c - r_1)(r_c - r_2)$$

- r_c is the the cavity radius, 1 and 2 indicate the electrons, μ_1 and μ_2 are variational parameters.

He in a spherical cavity

- The results are $\lesssim 2\%$ (except for radius 1.2).
- [1] and [3] are variational.
- [2] => fifth–order perturbation.

r_C	Present	Ref. [1]	Ref. [2]	Ref. [3]
0,9	2,5001	2,4670	2,4632	2,4633
1,0	1,03548	1,0183	1,0157	1,0158
1,2	−0,6879	−0,7079	−0,7088	−0,7087
1,5	−1,8756	−1,9061	−1,9069	−1,9067
2,0	−2,5510	−2,5998	−2,6040	−2,6036
4,0	−2,8462	−2,8931	−2,9005	−2,8997
5,0	−2,8531	−2,8978	−2,9034	−2,9028
6,0	−2,8553	−2,8990	−2,9036	−2,9033

[1] Banerjee, A.; Kamal, C.; Chowdhury, A. **Phys. Lett. A**, v.350, p. 121-125 (2006).
[2] Montgomery Jr., H.E.; Aquino, N.; Flores-Riveros, A. **Phys. Lett. A**, v.374, p. 2044-2047 (2010).
[3] Flores-Riveros, A.; Aquino, N.; Montgomery Jr., H.E. **Phys. Lett. A**, v.374, p. 1246 (2010).

He_2 in a cavity

- Trial function suggested is:

$$\psi_{He_2} = \psi_{H_2^+}(1)\alpha(\omega_1)\,\psi_{H_2^+}(2)\beta(\omega_2)\overline{\psi_{H_2^+}}(3)\alpha(\omega_3)\,\overline{\psi_{H_2^+}}(4)\beta(\omega_4) + \ldots$$

- The permutations are obtained from the determinant (Slater):

$$\psi_{He_2} = \begin{vmatrix} \psi_{H_2^+}(1)\alpha(\omega_1) & \psi_{H_2^+}(1)\beta(\omega_1) & \overline{\psi_{H_2^+}}(1)\alpha(\omega_1) & \overline{\psi_{H_2^+}}(1)\beta(\omega_1) \\ \psi_{H_2^+}(2)\alpha(\omega_2) & \psi_{H_2^+}(2)\beta(\omega_2) & \overline{\psi_{H_2^+}}(2)\alpha(\omega_2) & \overline{\psi_{H_2^+}}(2)\beta(\omega_2) \\ \psi_{H_2^+}(3)\alpha(\omega_3) & \psi_{H_2^+}(3)\beta(\omega_3) & \overline{\psi_{H_2^+}}(3)\alpha(\omega_3) & \overline{\psi_{H_2^+}}(3)\beta(\omega_3) \\ \psi_{H_2^+}(4)\alpha(\omega_4) & \psi_{H_2^+}(4)\beta(\omega_4) & \overline{\psi_{H_2^+}}(4)\alpha(\omega_4) & \overline{\psi_{H_2^+}}(4)\beta(\omega_4) \end{vmatrix}$$

$$\psi_{H_2^+} = 1s_A + 1s_B \qquad \overline{\psi_{H_2^+}} = 1s_A - 1s_B$$

He_2 in a cavity

$$\psi_{H_2^+} = 1s_A + 1s_B \qquad \overline{\psi_{H_2^+}} = 1s_A - 1s_B$$

- $\psi_{H_2^+}$ is the ground state eigenfunction for the ionized hydrogen molecule (molecular orbital) and $\overline{\psi_{H_2^+}}$ is antibound molecular orbital.
- $1s_{A,B}$ are the atomic trial functions for the atoms A and B.

He_2 in a cavity

- Geometry: prolate ellipsoidal cavity.
- Atomic nuclei => fixed at the foci of the ellipse.
- Elliptical coordinates:

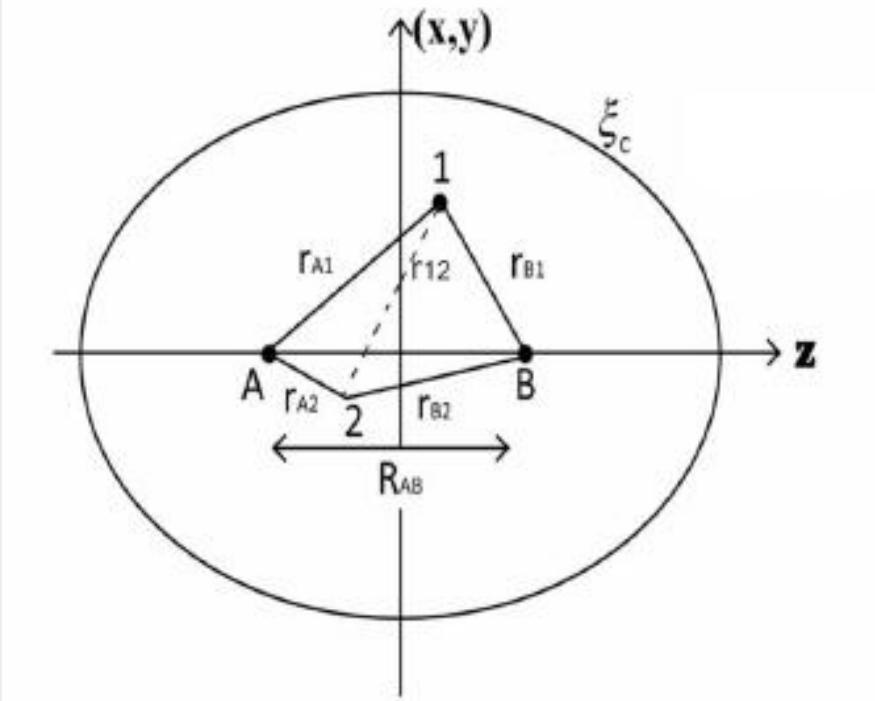
$$\xi_i = \frac{r_{A(i)} + r_{B(i)}}{R_{AB}}; \quad \eta_i = \frac{r_{A(i)} - r_{B(i)}}{R_{AB}}$$

$$1 < \xi < \xi_c; \; -1 < \eta < 1; \; 0 < \varphi < 2\pi$$

- *$1/\xi_c$ is the eccentricity of the ellipse.*

He_2 in a cavity

- Geometry:



H_2

He_2 in a cavity

- Molecular orbitals (prolate spherodal coordinates)*:

$$\psi_{H_2^+} = (\xi_c - \xi)\left[e^{-\mu(\xi+\eta)} + e^{-\mu(\xi-\eta)}\right]$$

$$\overline{\psi_{H_2^+}} = (\xi_c - \xi)\left[e^{-\mu(\xi+\eta)} - e^{-\mu(\xi-\eta)}\right]$$

- μ *is the variational parameter.*

* DA SILVA, J. F.; SILVA, F. R.; DRIGO FILHO, E. The effect of confinement on the electronic energy and polarizability of a hydrogen molecular ion. **International Journal of Quantum Chemistry**, v. 116, p. 497–503, 2016.

He_2 in a cavity

- Energy values:

$$\langle E_{He_2} \rangle = 2\left\langle \psi_{H_2^+} \middle| H_{H_2^+} \middle| \psi_{H_2^+} \right\rangle + 2\left\langle \overline{\psi_{H_2^+}} \middle| H_{H_2^+} \middle| \overline{\psi_{H_2^+}} \right\rangle + J11 + J22 + 4J12 - 2K12 + \frac{Z^2}{R}$$

- $H_{H_2^+}$ is the Hamiltonian for the ionized hydrogen molecule with Z = 2 and

$$J11 = \left\langle \psi_{H_2^+}(1)\psi_{H_2^+}(2) \middle| \frac{1}{r_{12}} \middle| \psi_{H_2^+}(1)\psi_{H_2^+}(2) \right\rangle \quad J22 = \left\langle \overline{\psi_{H_2^+}}(1)\overline{\psi_{H_2^+}}(2) \middle| \frac{1}{r_{12}} \middle| \overline{\psi_{H_2^+}}(1)\overline{\psi_{H_2^+}}(2) \right\rangle$$

$$J12 = \left\langle \psi_{H_2^+}(1)\overline{\psi_{H_2^+}}(2) \middle| \frac{1}{r_{12}} \middle| \psi_{H_2^+}(1)\overline{\psi_{H_2^+}}(2) \right\rangle \quad K12 = \left\langle \psi_{H_2^+}(1)\overline{\psi_{H_2^+}}(2) \middle| \frac{1}{r_{12}} \middle| \overline{\psi_{H_2^+}}(1)\psi_{H_2^+}(2) \right\rangle$$

He_2 in a cavity

- In the calculation, it is used*:

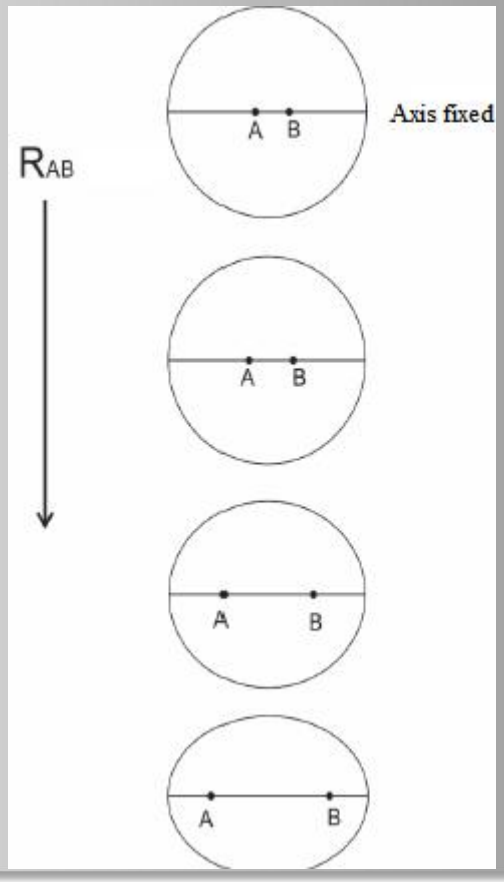
$$\frac{1}{r_{12}} = \frac{2}{R_{AB}} \sum_{k=0}^{\infty} (2k+1) P_k(\xi_<) Q_k(\xi_>) P_k(\eta_1) P_k(\eta_2)$$

- P_k and Q_k are the first and second species Laguerre polynom.
- The energy values are obtained from variational calculation of $\langle H_{H_2^+} \rangle$.

*SLATER, J. C. **Quantum Theory of Molecules and Solids: Electronic structure of molecules.** 1 ed. [s.l.] McGraw-Hill, 1963. v. 1

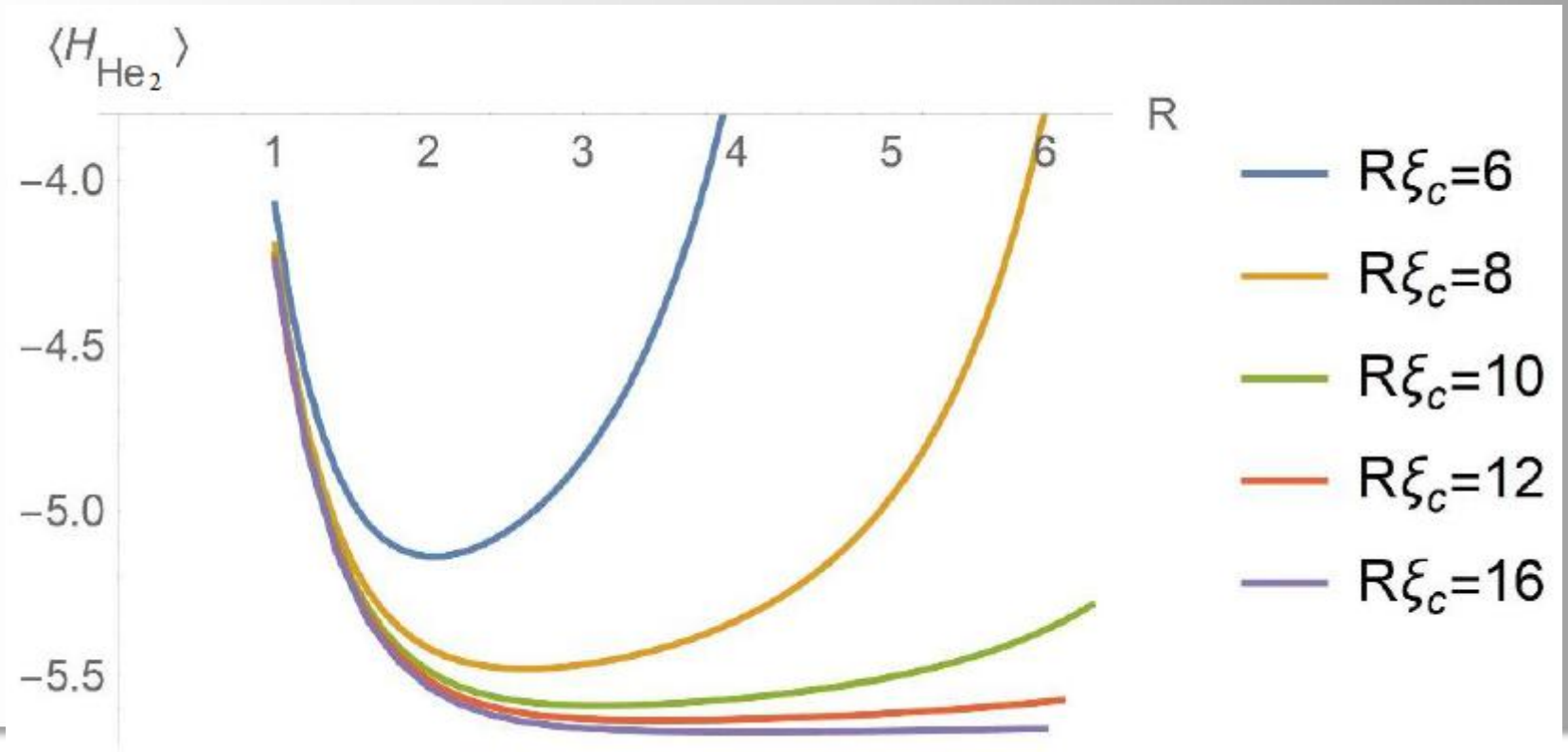
Results

- Energy $\langle E_{He_2} \rangle$ as a function of the distance between nuclei, R.
- confinement parameter is the major axis of the ellipsoid, $R\xi_c$.
- R_{eq} are the nuclei distances for minimum value of energy for each value of major axis.



Results

- $\langle E_{He_2} \rangle$ x R



Results

- The energy for He_2 is compared to the energy of two He atoms in a cavity of the same geometry.
- The mean energy for the helium atom, $\langle E_{He} \rangle$, is obtained fixing the nucleus on one focus.
- The trial function for the helium atom is:

$$\Psi = (\xi_c - \xi_1)(\xi_c - \xi_2)\left[e^{-\mu(\xi_1+\eta_1)} - \mu(\xi_2+\eta_2)\right]$$

Results

- Table comparing the molecule with two non-interacting atoms.

$R\xi_c$	R_{eq}	$\langle E_{He_2} \rangle$	$2\langle E_{He} \rangle$	$\langle E_{He_2} \rangle$-$2\langle E_{He} \rangle$
6	2.0310	-5.13775	-4.91444	-0.223
8	2.6254	-5.47722	-5.34155	-0.135
10	3.10621	-5.58799	-5.50468	-0.083
12	3.48903	-5.6335	-5.57946	-0.054
16	4.0169	-5.66781	-5.64147	-0.026

Conclusions

- We note that the trial function inspired in the SUSY formalism is suitable to be used in variational calculation for confined systems.
- The results for He atom ground state energies are close to the other present in the literature.
- Results for He_2 molecule suggested it is possible to obtain a chemical bound from the quantum confinement.

- Financial support

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