Positronium molecules

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Positronium molecules

- What?
  - Ps_N: system formed by N electrons and N positrons
- Why?
  - Ps and Ps_2 are known to be bound, the latter has been detected experimentally recently
  - But we don't know about Ps_3, Ps_4 ...
  - Interesting soft binding mechanisms not present in “normal” molecules; interesting wfns required
- How?
  - Build and understand wfn for N=2, generalize

Wave function framework

- Wave function form: $\Psi = \Psi_S e^J$
  - Ψ_S ***enforces*** (anti-)symmetries and boundary conditions
  - e^J ***respects*** (anti-)symmetries and boundary conditions

Similar systems

- Ps_2 can be compared with H_2

- Data to bear in mind:

	E (a.u.)	E dissoc. (a.u.)
Ps_2	-0.5160038	-0.5000000
H_2 (B-O)	-1.1744757	-1.0000000
H_2 (quantum)	-1.1649958	-1.0000000

H_2 wave function

- For H_2 one could use
  - $\Psi_S = \left(\phi(1\mathrm{a}) + \phi(1\mathrm{b})\right)\left(\phi(2\mathrm{a}) + \phi(2\mathrm{b})\right)$
- Breaks the electron-positron symmetry for Ps_2
- Instead, try the simpler
  - $\Psi_S = \phi(1\mathrm{a})\,\phi(2\mathrm{b}) + \phi(1\mathrm{b})\,\phi(2\mathrm{a})$

  (neglecting two-electron-one-ion terms)

H_2 wave function

- Results:

	Jastrow	E (a.u.)	% E_b
H_2 (B-O)	U	-1.1708(1)	97.89(6)
H_2 (B-O)	U+H	-1.174401(8)	99.957(5)
H_2 (quantum)	U	-1.1579(1)	95.70(6)
H_2 (quantum)	U+H	-1.16369(2)	99.21(1)

Ps_2 fails to bind with this wave function

Biexciton wave function

- The 2D biexciton problem is similar to this one
- Wave function:

$$\Psi_S = \exp\left(\frac{c_5 r_{1a} + c_6 r_{1a}^2}{1 + c_7 r_{1a}} + \frac{c_5 r_{1b} + c_8 r_{1b}^2}{1 + c_9 r_{1b}} + \frac{c_5 r_{2a} + c_8 r_{2a}^2}{1 + c_9 r_{2a}} + \frac{c_5 r_{2b} + c_6 r_{2b}^2}{1 + c_7 r_{2b}}\right) +$$
$$\exp\left(\frac{c_5 r_{1a} + c_8 r_{1a}^2}{1 + c_9 r_{1a}} + \frac{c_5 r_{1b} + c_6 r_{1b}^2}{1 + c_7 r_{1b}} + \frac{c_5 r_{2a} + c_6 r_{2a}^2}{1 + c_7 r_{2a}} + \frac{c_5 r_{2b} + c_8 r_{2b}^2}{1 + c_9 r_{2b}}\right)$$

- That is,

$$\Psi_S = \exp\left[u_1(1a) + u_2(1b) + u_2(2a) + u_1(2b)\right]\phi_1(1a)\phi_2(1b)\phi_2(2a)\phi_1(2b) +$$
$$\exp\left[u_2(1a) + u_1(1b) + u_1(2a) + u_2(2b)\right]\phi_2(1a)\phi_1(1b)\phi_1(2a)\phi_2(2b)$$

Biexciton wave function

- By neglecting the different Jastrow-like terms,

$$\Psi_S = \phi_1(1a)\phi_2(1b)\phi_2(2a)\phi_1(2b) + \phi_2(1a)\phi_1(1b)\phi_1(2a)\phi_2(2b)$$

- NB, the Jastrow factor will be added on top

Biexciton wave function

- Results:

	Jastrow	E (a.u.)	% E_b
H_2 (B-O)	U	-1.1706(1)	97.78(6)
H_2 (B-O)	U+H	-1.174408(8)	99.961(5)
H_2 (quantum)	U	-1.1583(1)	95.94(6)
H_2 (quantum)	U+H	-1.16392(2)	99.348(6)
Ps_2	U	-0.5136(2)	85(1)
Ps_2	U+H	-0.515866(8)	99.14(5)

Generalizing

$$\Psi_S = \phi_1(1a)\phi_2(1b)\phi_2(2a)\phi_1(2b) + \phi_2(1a)\phi_1(1b)\phi_1(2a)\phi_2(2b)$$

- Interpretation:
  - Φ_1 represents electron-positron binding
  - Φ_2 represents Ps-Ps binding

Generalization

- Ps_2 wave function:

$$\Psi_S = \phi_1(r_{11})\phi_2(r_{12})\phi_2(r_{21})\phi_1(r_{22}) + \\ + \phi_2(r_{11})\phi_1(r_{12})\phi_1(r_{21})\phi_2(r_{22})$$

- Interpretation:
  - Φ_1 represents electron-positron binding
  - Φ_2 represents Ps-Ps binding
- Extension:
  - Wave function is a sum of terms
  - Each term is a product of pairing functions for all electron-positron pairs

Generalization

- Generalization:

$$\Psi_S = \sum_{n=1}^{N_T} c_n \prod_{e,p}^{N} \phi_{\lambda_{ep}^{(n)}}(r_{ep})$$

- Where:
  - c_n are the term coefficients, some of which are related by symmetry
  - $\underline{\underline{\lambda}}^{(n)}$ is the matrix of pairing-function selectors for the n-th term, or *"wave function constructor"*
  - Terms related by symmetry can be (and are) generated automatically

Example: Ps_2

- E.g. for Ps_2:

$$\Psi_S = \sum_{n=1}^{N_T} c_n \prod_{e,\,p}^{N} \phi_{\lambda_{ep}^{(n)}}(r_{ep}) \quad \rightarrow \quad N_T = 2 \quad \begin{cases} c_1 = 1 & \underline{\lambda}^{(1)} = \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix} \\ c_2 = 1 & \underline{\lambda}^{(2)} = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix} \end{cases}$$

gives:

$$\Psi_S = \phi_1(r_{11})\phi_2(r_{12})\phi_2(r_{21})\phi_1(r_{22}) + \\ + \phi_2(r_{11})\phi_1(r_{12})\phi_1(r_{21})\phi_2(r_{22})$$

- In practice we need not specify the second term since it is related to the first by symmetry

Dissociated Ps_3

- To describe Ps_2+Ps:

$$\underline{\underline{\lambda}}^{(1)} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \\ 3 & 3 & 1 \end{pmatrix} \qquad \underline{\underline{\lambda}}^{(2)} = \begin{pmatrix} 2 & 1 & 3 \\ 1 & 2 & 3 \\ 3 & 3 & 1 \end{pmatrix}$$

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- Total: 8 terms
- Φ_3 is a long-ranged pairing function

Dissociated Ps_4

- To describe Ps_2+Ps_2:

$$\underline{\underline{\lambda}}^{(1)} = \begin{pmatrix} 1 & 2 & 3 & 3 \\ 2 & 1 & 3 & 3 \\ 3 & 3 & 1 & 2 \\ 3 & 3 & 2 & 1 \end{pmatrix} \qquad \underline{\underline{\lambda}}^{(2)} = \begin{pmatrix} 1 & 3 & 2 & 3 \\ 3 & 2 & 3 & 1 \\ 2 & 3 & 1 & 3 \\ 3 & 1 & 3 & 2 \end{pmatrix}$$

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- Total: 32 terms
- Φ_3 is a long-ranged pairing function

Further work needed...

- For a variety of sensible constructors, the wave function does not seem capable of describing bound Ps_3 and Ps_4 (yet!)
- Backflow is ready to be used
- Most likely, need 4-body Jastrow