A VMC study of the isotopologues of H_2 and H_2^+

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Outline

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Why do molecular structure calculations?

- Compare results predicted by theoretical models with high-resolution spectroscopic measurements.
- Currently need to include very accurate description of correlation, relativistic and QED effects, and finite size nuclei, to agree with most recent experiments.
- Prediction of quantities that have yet to be measured.
- Benchmarking - total nonrelativistic energy.

Coulomb Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \frac{1}{2}\sum_A \frac{\nabla_A^2}{M_A} - \sum_{i,\,A} \frac{Z_A}{|\mathbf{r}_i - \boldsymbol{\tau}_A|}$$

$$+ \sum_{i,\,j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{A,\,B>A} \frac{Z_A Z_B}{|\boldsymbol{\tau}_A - \boldsymbol{\tau}_B|}\,,$$

Born-Oppenheimer approximation

- Trial wave function:

$$\Psi_n(\mathbf{r}, \boldsymbol{\tau}) = \sum_k \phi_{k,n}(\boldsymbol{\tau}) \, \chi_k(\mathbf{r}; \boldsymbol{\tau})$$

- Equation of motion for nuclei:

$$\left[-\frac{1}{2} \sum_A \frac{\nabla_A^2}{M_A} + \epsilon_k(\boldsymbol{\tau}) \right] \phi_{k,n}(\boldsymbol{\tau}) = E_n \, \phi_{k,n}(\boldsymbol{\tau}).$$

- Diatomic molecule:

$$\left[-\frac{1}{2\mu} \frac{\mathsf{d}^2}{\mathsf{d}\tau^2} + V(\tau) + \frac{J(J+1)}{2\mu\tau^2} \right] \phi_{\nu,J}(\tau) = E_{\nu,J} \, \phi_{\nu,J}(\tau),$$

Nonadiabatic molecular structure calculations

- Alternative approach - abandon idea of separating the electronic and nuclear motion - automatically include all corrections to BO approximation.
- First such results obtained by Kolos and Wolniewicz in 1964 (J. Chem. Phys. **41**, 3674).
- Recent calculations for small atoms and diatomic molecules (e.g. J. Chem. Phys. **113**, 4203) have used the Ritz variational method to optimize a wave function of the form

$$\Psi(\mathbf{r}, \boldsymbol{\tau}) = \sum_k c_k \phi_k(\mathbf{r}, \boldsymbol{\tau}) \,,$$

where the c_k are linear coefficients and the ϕ_k are explicitly correlated Gaussians.

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VMC in one slide

- Variational Monte Carlo (VMC) is a method for evaluating quantum mechanical expectation values which is based on a combination of the variational principle and Monte Carlo integration.

- Variational principle:

$$E_{\mathsf{V}} = \frac{\int \Psi_{\mathsf{T}}^*(\mathbf{R})\, \hat{H}\, \Psi_{\mathsf{T}}(\mathbf{R})\, \mathsf{d}\mathbf{R}}{\int \Psi_{\mathsf{T}}^*(\mathbf{R})\, \Psi_{\mathsf{T}}(\mathbf{R})\, \mathsf{d}\mathbf{R}} \geq E_0$$

- Monte Carlo integration:

$$E_{\mathsf{V}} = \frac{\int |\Psi_{\mathsf{T}}(\mathbf{R})|^2\, [\Psi_{\mathsf{T}}(\mathbf{R})^{-1}\, \hat{H}\, \Psi_{\mathsf{T}}(\mathbf{R})]\, \mathsf{d}\mathbf{R}}{\int |\Psi_{\mathsf{T}}(\mathbf{R})|^2\, \mathsf{d}\mathbf{R}}$$

Wave function optimization

- Optimize a trial wave function containing a set of parameters $\{\alpha\}$ by minimizing the value of a cost function with respect to the values of the parameters.

- Unreweighted variance minimization

$$\sigma_{\mathsf{U}}^2(\alpha) = \frac{1}{N_C - 1} \sum_{n=1}^{N_C} \left| E_{\mathsf{L}}^{\alpha}(\mathbf{R}_n) - \frac{1}{N_C} \sum_{n=1}^{N_C} E_{\mathsf{L}}^{\alpha}(\mathbf{R}_n) \right|^2$$

- Energy minimization

$$\Psi_{\mathsf{T}}^{\alpha_{n+1}}(\mathbf{R}) \approx \Psi_{\mathsf{T}}^{\alpha_n}(\mathbf{R}) + \sum_{i=1}^{p} \frac{\partial \Psi_{\mathsf{T}}^{\alpha_n}(\mathbf{R})}{\partial \alpha_n^i} \, \delta\alpha_n^i$$

$$\frac{\partial}{\partial \alpha_{n+1}^i} \frac{\int d\mathbf{R} \, [\Psi_{\mathsf{T}}^{\alpha_{n+1}}(\mathbf{R})]^* \hat{H} \Psi_{\mathsf{T}}^{\alpha_{n+1}}(\mathbf{R})}{\int d\mathbf{R} |\Psi_{\mathsf{T}}^{\alpha_{n+1}}(\mathbf{R})|^2} = 0 \quad \forall \, i$$

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Pairing-Jastrow wave function

- Combination of pairing orbitals describing interactions between oppositely charged electrons and nuclei, all multiplied by a Jastrow factor.

$$\Psi_{PJ}(\mathbf{R}) = e^{J(\mathbf{R})} \Psi_P(\mathbf{R})$$

- Example pairing wave function for H_2:

$$\Psi_P(\mathbf{R}) = \psi_\alpha(r_{1A})\psi_\beta(r_{1B})\psi_\alpha(r_{2B})\psi_\beta(r_{2A})$$
$$+ \psi_\alpha(r_{1B})\psi_\beta(r_{1A})\psi_\alpha(r_{2A})\psi_\beta(r_{2B})$$

$$\psi_\lambda(r) = e^{-r^2/(a_\lambda(b_\lambda + r))}$$

Generalized Jastrow factor

$$J(\mathbf{R}) = J_{\text{2-body}}(\mathbf{R}) + J_{\text{3-body}}(\mathbf{R}) + J_{\text{4-body}}(\mathbf{R})$$

$$J_{n\text{-body}}(\mathbf{R}) = \sum_{\mathcal{N}} \sum_{\{\mu_{\mathcal{N}}\}}^{q_n} c_{\{\mu_{\mathcal{N}}\}} \Phi_{\{\mathcal{N}\}}^{\{\mu_{\mathcal{N}}\}},$$

$$\sum_{\{\mu_{\mathcal{N}}\}} = \sum_{\mu_1=0}^{q_n} \sum_{\mu_2=0}^{q_n} .... \sum_{\mu_p=0}^{q_n}$$

$$c_{\{\mu_{\mathcal{N}}\}} = c_{\mu_1 \mu_2 .... \mu_p}$$

$$\Phi_{\{\mathcal{N}\}}^{\{\mu_{\mathcal{N}}\}} = \Phi_1^{\mu_1}(\mathbf{r}_1) \Phi_2^{\mu_2}(\mathbf{r}_2) .... \Phi_p^{\mu_p}(\mathbf{r}_p)$$

- See López Ríos et al. (Phys. Rev. E **86**, 036703) for more details and examples.

Natural powers

$$\Phi_i^\mu(\mathbf{r}) = (1 - r/L_i)^D \, \Theta(L_i - r) \, r^\mu$$

Jastrow	Expansion Order	Energy (a.u.)	% E_B
2-body	6	$-1.15922(4)$	$97.08(2)$
2-body	6		
3-body	3	$-1.163842(8)$	$99.889(5)$

▶ Four-body effects important when using pairing wave function to calculate H_2 energy with static nuclei (J. Chem. Phys. **130**, 134103).

Boys-Handy indexing

$$\mu_1 + \mu_2 + ... + \mu_p \leq q_n$$

$$\Phi_i^\mu(\mathbf{r}) = \left(\frac{r}{r + l_i} \right)^\mu$$

Jastrow	Expansion Order (Boys-Handy)	Energy (a.u.)	$\% \, E_B$
4-body	6	$-1.164007(6)$	$99.989(4)$

▶ Two-body and three-body effects included automatically.

Cusp conditions

- Coulomb potential diverges when any two charged particles coalesce.
- For eigenstate to satisfy Schrödinger equation, kinetic energy must diverge to cancel out potential energy.
- Exact wave function obeys cusp conditions

$$\left(\frac{1}{\Psi} \frac{\partial \hat{\Psi}}{\partial r_{ij}} \right)_{r_{ij} \to 0} = \frac{2 \, q_i q_j \mu_{ij}}{3 \pm 1}$$

- Usually we enforce the cusp conditions on the trial wave function.

Alexander-Coldwell pairing functions

$$\Psi_P(\mathbf{R}) = \psi_\alpha(r_{1A})\psi_\beta(r_{2B}) + \psi_\alpha(r_{1B})\psi_\beta(r_{2A})$$
$$+ \psi_\alpha(r_{2A})\psi_\beta(r_{1B}) + \psi_\alpha(r_{2B})\psi_\beta(r_{1A})$$

$$\psi_\lambda = e^{-a_\lambda r}$$

- Previously used in conjunction with non-standard sampling in VMC (J. Chem. Phys. **129**, 114306).
- The a_λ are freely optimizable if we waive the electron-nucleus cusp conditions.
- Also waive electron-electron cusp conditions (Jastrow factor) and minimize unreweighted variance - get lower energy for H_2!

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H$_2$ isotopologues

Molecule	Exact energy (a.u.)	VMC energy (a.u.)
H$_2$	-1.1640250308	$-1.1640250(1)$
HD	-1.1654719220	$-1.1654718(1)$
HT	-1.16600201	$-1.1660017(1)$
D$_2$	-1.1671688092	$-1.1671686(1)$
DT	-1.16781963	$-1.1678195(1)$
T$_2$	-1.1685356757	$-1.1685354(1)$

- Exact results from Bubin et al. (Chem. Phys. Lett. **477**, 12, Phys. Rev. A **83**, 042520, and J. Chem. Phys. **135**, 074110).

H_2^+ isotopologues

Ion	Exact energy (a.u.)	VMC energy (a.u.)
H_2^+	$-0.5971390631234050747\,4$	$-0.597139070(5)$
HD^+	-0.59789796864503622	$-0.597897971(6)$
HT^+	-0.5981761346697657	$-0.598176135(6)$
D_2^+	$-0.5987887843306834644\,8$	$-0.598788774(5)$
DT^+	-0.59913066285506164	$-0.599130660(6)$
T_2^+	-0.59950691011154145	$-0.599506885(5)$

▶ Exact results from Frolov (J. Phys. B **35**, L331).

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Conclusions

- Get very accurate results for H_2 and H_2^+ with VMC when waiving cusp conditions and optimizing the wave function with unreweighted variance minimization.
- So far not easily extendable to H_3+ etc.
- Can we apply anything of what we have learnt to solid hydrogen with zero point motion?

A wave function for solid hydrogen

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \, \Psi_{\mathsf{N}}(\boldsymbol{\tau}) \, \Psi_{\mathsf{S}}(\mathbf{R}) \,,$$

$$\Psi_{\mathsf{N}}(\boldsymbol{\tau}) = \prod_{A=1}^{2n} \chi_A(\boldsymbol{\tau}_A - \boldsymbol{\tau}_A^{\mathsf{eq}})$$

$$\Psi_{\mathsf{S}} = \begin{vmatrix} \psi(\mathbf{r}_1, \tilde{\mathbf{r}}_1; \boldsymbol{\tau}) & \psi(\mathbf{r}_1, \tilde{\mathbf{r}}_2; \boldsymbol{\tau}) & \ldots & \psi(\mathbf{r}_1, \tilde{\mathbf{r}}_n; \boldsymbol{\tau}) \\ \psi(\mathbf{r}_2, \tilde{\mathbf{r}}_1; \boldsymbol{\tau}) & \psi(\mathbf{r}_2, \tilde{\mathbf{r}}_2; \boldsymbol{\tau}) & \ldots & \psi(\mathbf{r}_2, \tilde{\mathbf{r}}_n; \boldsymbol{\tau}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi(\mathbf{r}_n, \tilde{\mathbf{r}}_1; \boldsymbol{\tau}) & \psi(\mathbf{r}_n, \tilde{\mathbf{r}}_2; \boldsymbol{\tau}) & \ldots & \psi(\mathbf{r}_n, \tilde{\mathbf{r}}_n; \boldsymbol{\tau}) \end{vmatrix}$$

$$\psi(\mathbf{r}_i, \tilde{\mathbf{r}}_j; \boldsymbol{\tau}) = \sum_{A=1}^{2n} \sum_{B>A} \Phi(\mathbf{r}_i, \tilde{\mathbf{r}}_j, \boldsymbol{\tau}_A, \boldsymbol{\tau}_B)$$

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