PROJECT: Diagrammatic Multiplet-Sum Method (MSM) Density-Functional Theory (DFT): III. Inclusion of Relaxation and Application to LiH

- Learn more about dynamic, static, and nondynamic correlation in quantum chemistry while using deMon2k
- Be part of an on-going research project
- Deepen your formal understanding and see how you can contribute using only your personal computer (and lots of patience)

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ASESMA
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10 min

Dynamic correlation: When a single-determinant is good first approximation to the Wave function. *This is where conventional DFT works best.*

Static correlation: When the best single-determinant first approximation wave functions are energetically degenerate (because of symmetry). *Normal MSM DFT often works well here.*

Nondynamic correlation: When the best single-determinants are energetically quasidegenerate (typical of bond making and breaking). *Try to approach this via diagrammatic MSM DFT.*

These are fuzzy, but beautiful (and useful) ideas.

French impressionism. Claude Monet, ”Impression, sunrise” 1872.

* According to Bartlett and Stanton, “Applications of post-Hartree-Fock methods: A tutorial”, *Rev. Comput. Chem.* **5**, 65 (1994).

Combine the best from DFT with the best from wave function theory (WFT).

DFT is best for describing dynamic correlation.

WFT is best for strong correlation (static and nondynamic).

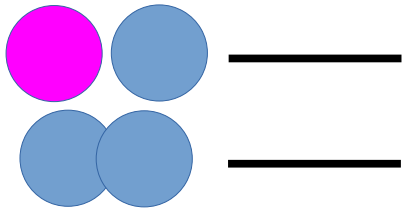
Want a *compact* multideterminantal (MDET) wave function.

Configuration Interaction (CI) expansion

$$\Psi = \Phi + \sum_{i,a} \Phi_i^a C_i^a + \sum_{i,j}^{a,b} \Phi_{i,j}^{a,b} C_{i,j}^{a,b} + \cdots$$

The fewer terms the better!

Case of H_2



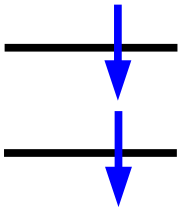
$$a = \sigma_u = \frac{1}{\sqrt{2(1-S)}}\left(s_A - s_B\right)$$

$$i = \sigma_g = \frac{1}{\sqrt{2(1+S)}}\left(s_A + s_B\right)$$

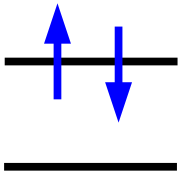
The overlap matrix $S = \langle s_A | s_B \rangle$

is used by chemists as one measure of bonding.

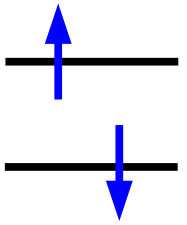
Possible fillings:



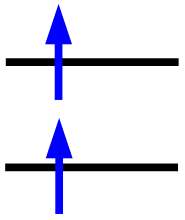
$|\bar{a}\,\bar{i}|$



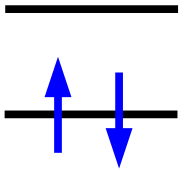
$|a\,\bar{a}|$



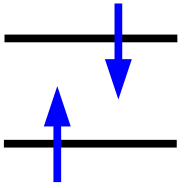
$|i\,\bar{a}|$



$|i\,a|$



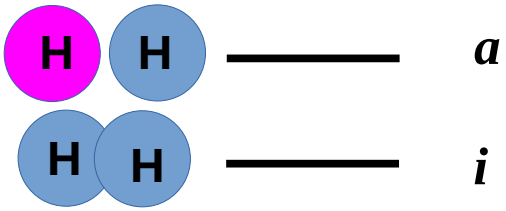
$|i\,\bar{i}|$



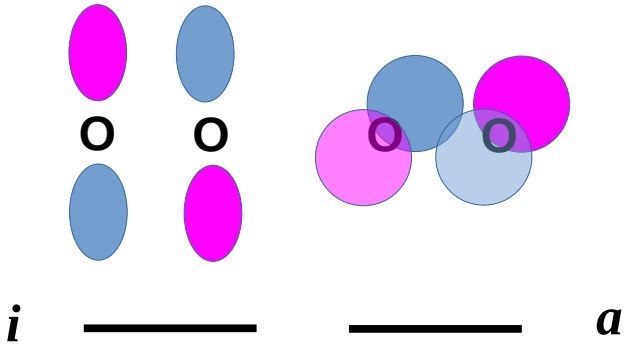
$|a\,\bar{i}|$

TOTEM IS VERSITILE

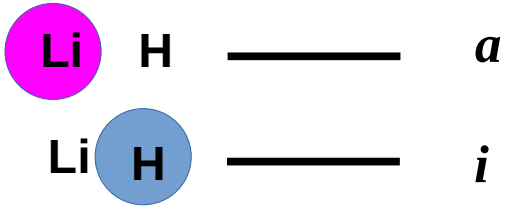
Case of H_2



Case of O_2



Case of LiH



$$M_S = 0 \Rightarrow \quad \Psi = |i\,\bar{i}|\,C_0 + |a\,\bar{i}|\,C_i^a + |i\,\bar{a}|\,C_{\bar{i}}^{\bar{a}} + |a\,\bar{a}|\,C_{i\,\bar{i}}^{a\,\bar{a}} \qquad \textbf{(1)}$$

$$\begin{bmatrix} E_0 & D & D & B \\ D & E_M & A & C \\ D & A & E_M & C \\ B & C & C & E_D \end{bmatrix} \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{i\,\bar{i}}^{a\,\bar{a}} \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{i\,\bar{i}}^{a\,\bar{a}} \end{pmatrix} \qquad \textbf{(2)}$$

Dynamic correlation terms easily obtained from DFT

$$E_0 = E[i\,\bar{i}] \qquad E_T = E[i\,a] = E[\bar{i}\,\bar{a}] \qquad E_M = E[a\,\bar{i}] = E[i\,\bar{a}] \qquad E_D = E[a\,\bar{a}] \qquad \textbf{(3)}$$

Static correlation term easily obtained from MSM DFT*

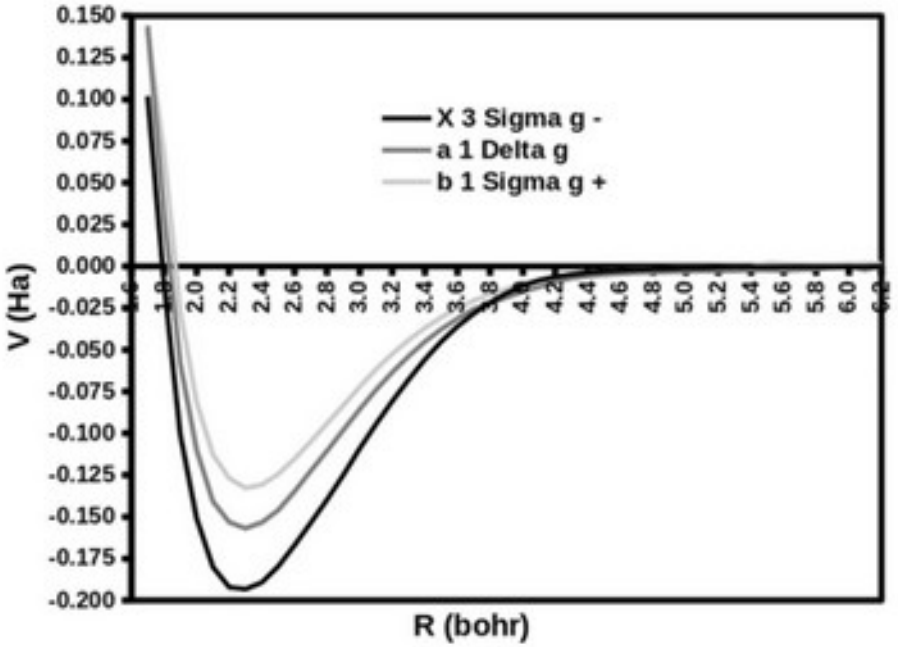
$$A = E_M - E_T \qquad \textbf{(4)}$$

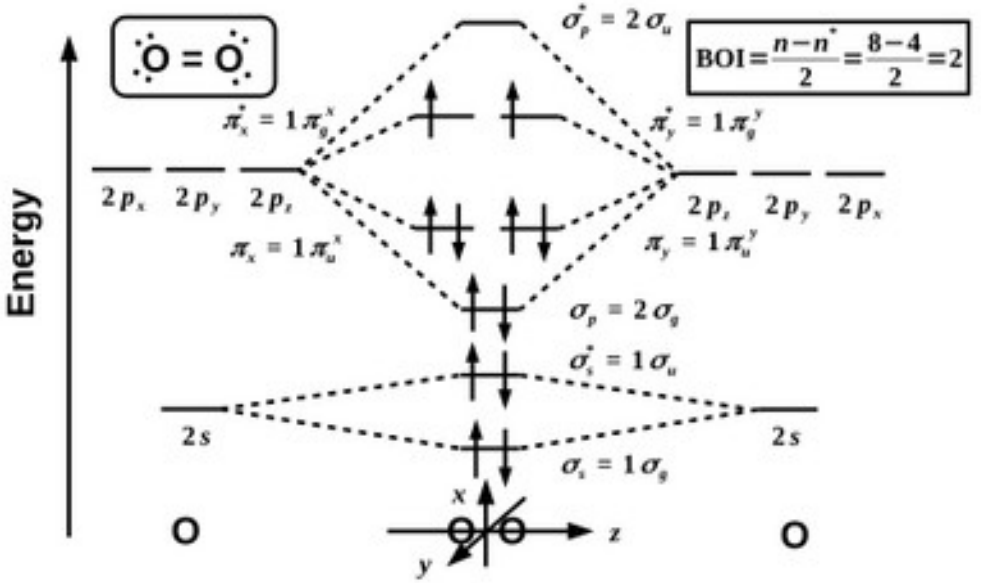
Formulae for *C* and *D* can be guessed from diagrammatic MSM DFT.

$$B = A \quad \textbf{(5)} \qquad C = -D = F_{i,a}[\mathrm{ENS}] \quad \textbf{(6)} \qquad \mathrm{ENS} \Rightarrow n_i = n_{\bar{i}} = n_a = n_{\bar{a}} \quad \textbf{(7)}$$

* T. Ziegler, A. Rauk, and E.J. Baerends, *Theor. Chim. Acta.* **4**, 877 (1977).

[PEMC21] A. Ponra, **A.J. Etindele**, **O. Motapon**, and **M.E. Casida**, "Practical Treatment of Singlet Oxygen with Density-Functional Theory and the Multiplet-Sum Method", *Theo. Chem. Acc.* **140**, 154 (2021).





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Diagrammatic MSM DFT H_2

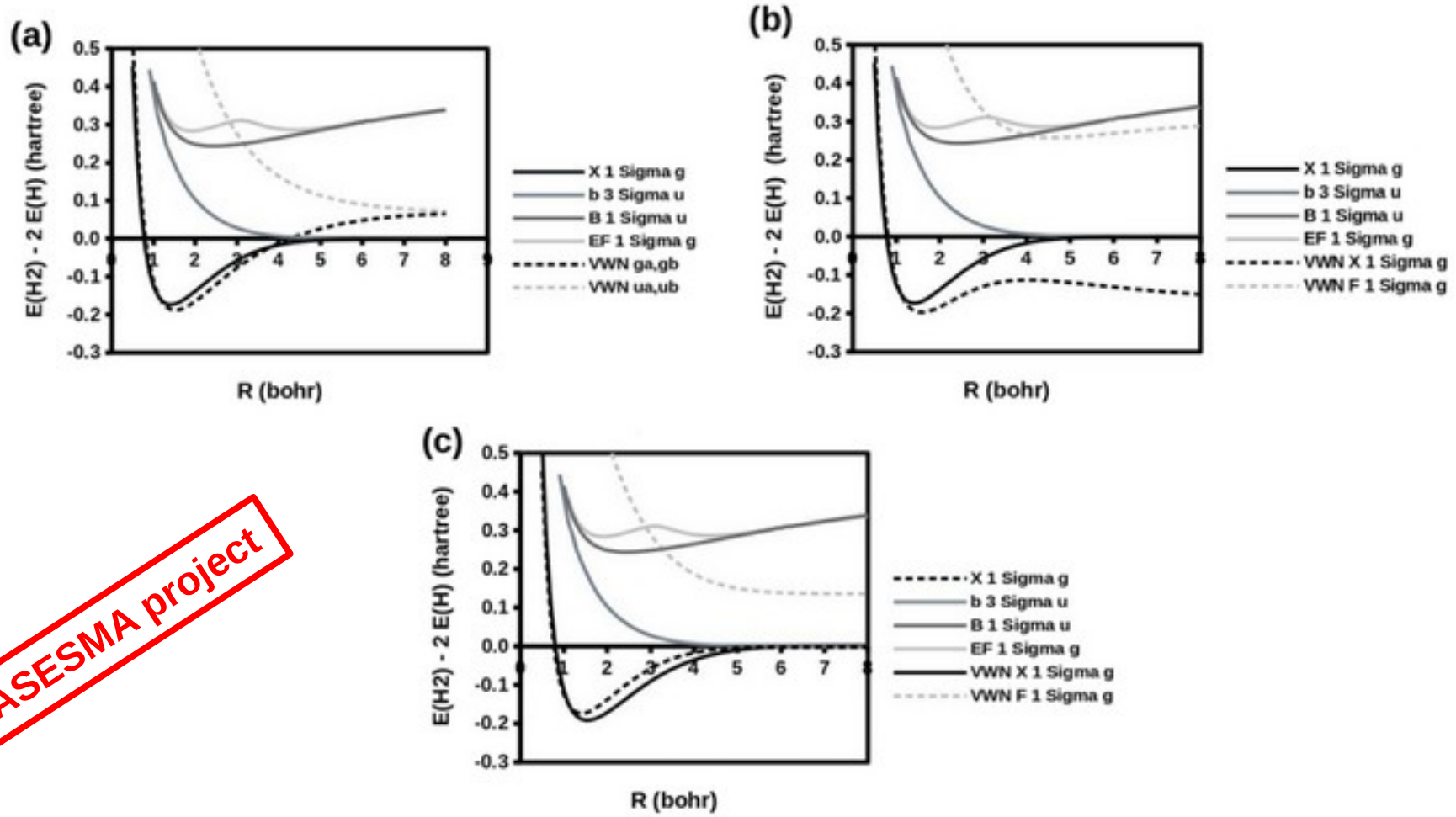

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FIG. 18. Three ways to calculate MSM $X\ ^1\Sigma_g$ and $F\ ^1\Sigma_g$ PECs: (a) VWN single-determinantal energies, (b) VWN single-determinantal energies corrected using the HF $B = A$, and (c) VWN single-determinantal energies obtained using B = VWN A.

[PBEC23] A. Ponra, **C. Bakasa**, **A.J. Etindele**, and **M.E. Casida**, "Diagrammatic Multiplet-Sum Method (MSM) Density-Functional Theory (DFT): Investigation of the Transferability of Integrals in ``Simple'' DFT-Based Approaches to Multi-Determinantal Problems'', *J. Chem. Phys.* **159**, 244306 (2023).

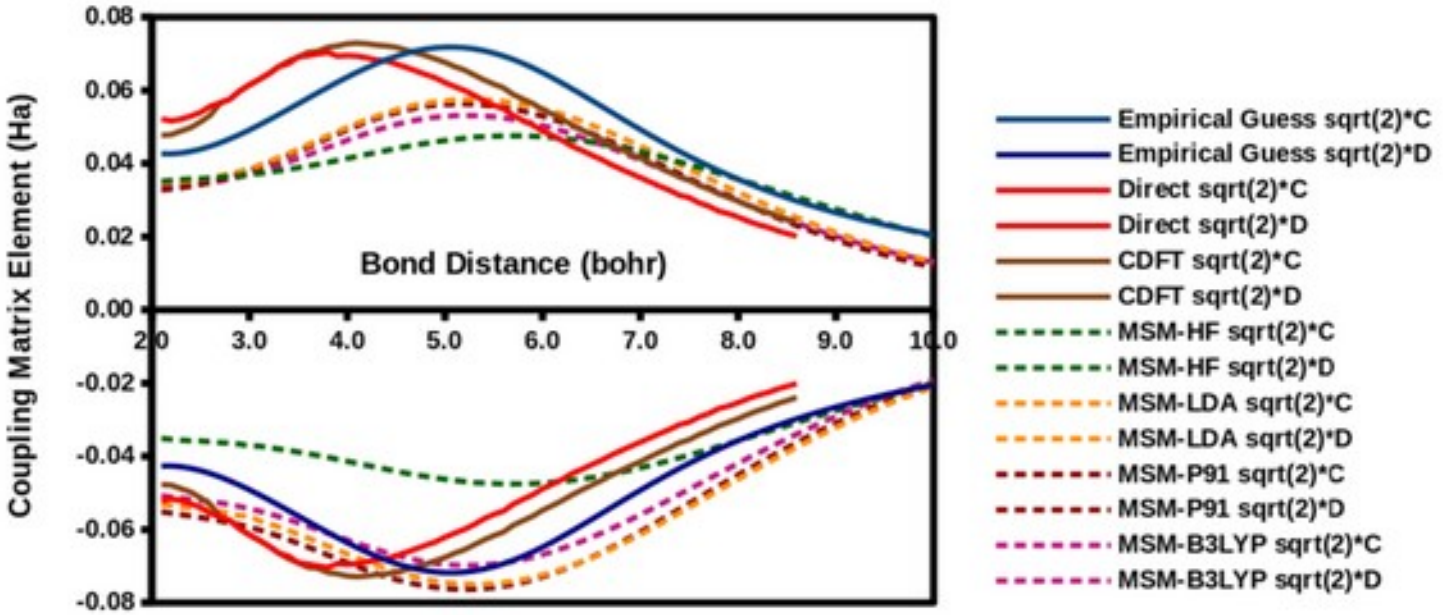

FIG. 11. Graph of the $\sqrt{2}C > 0$ and $\sqrt{2}D < 0$ matrix elements obtained from MSM-DFT. The empirical curves are a Gaussian guess at the coupling matrix element made in the supplementary material of Article I. The "direct" and "CDFT" curves were obtained from Fig. 30 of Ref. 21 after digitization with WEBPLOTDIGITIZER[37] and conversion to the format shown here. [The details of how these last two curves were calculated have not been published but we have confirmed the essential points of their calculations with one of the authors (TV) in order to be able to make the present comparison.]

[CPBE25] M.E. Casida, **A. Ponra**, **C. Bakasa**, and **A.J. Etindele**, "Diagrammatic Multiplet-Sum Method (MSM) Density-Functional Theory (DFT): Completion of the Two-Orbital Two-Electron Model (TOTEM) with an Application to the Avoided Crossing in Lithium Hydride (LiH)" *J. Chem. Phys*. **162**, 144317 (2025),

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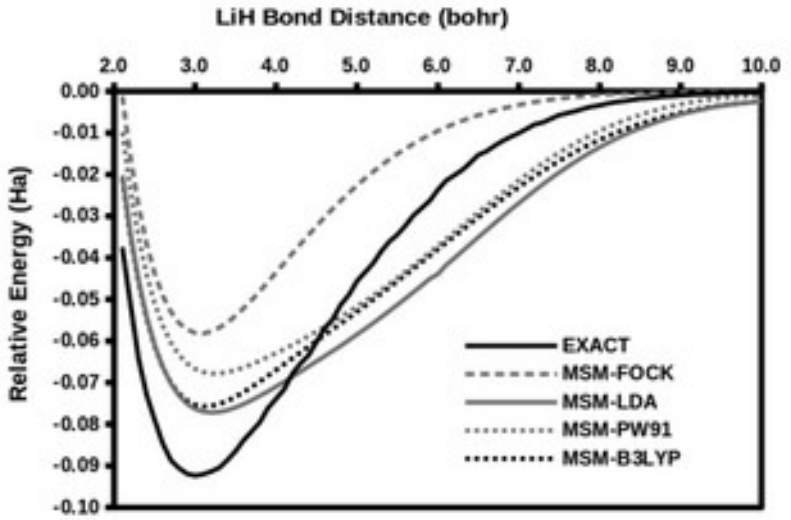


FIG. 13. Comparison of the EXACT $X\ ^1\Sigma$ and diagrammatic MSM PECs obtained with different DFAs using the *unsymmetrized* coupling matrix element.

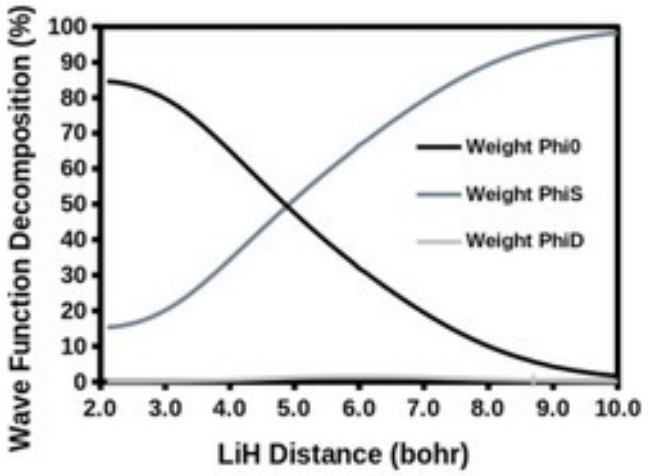
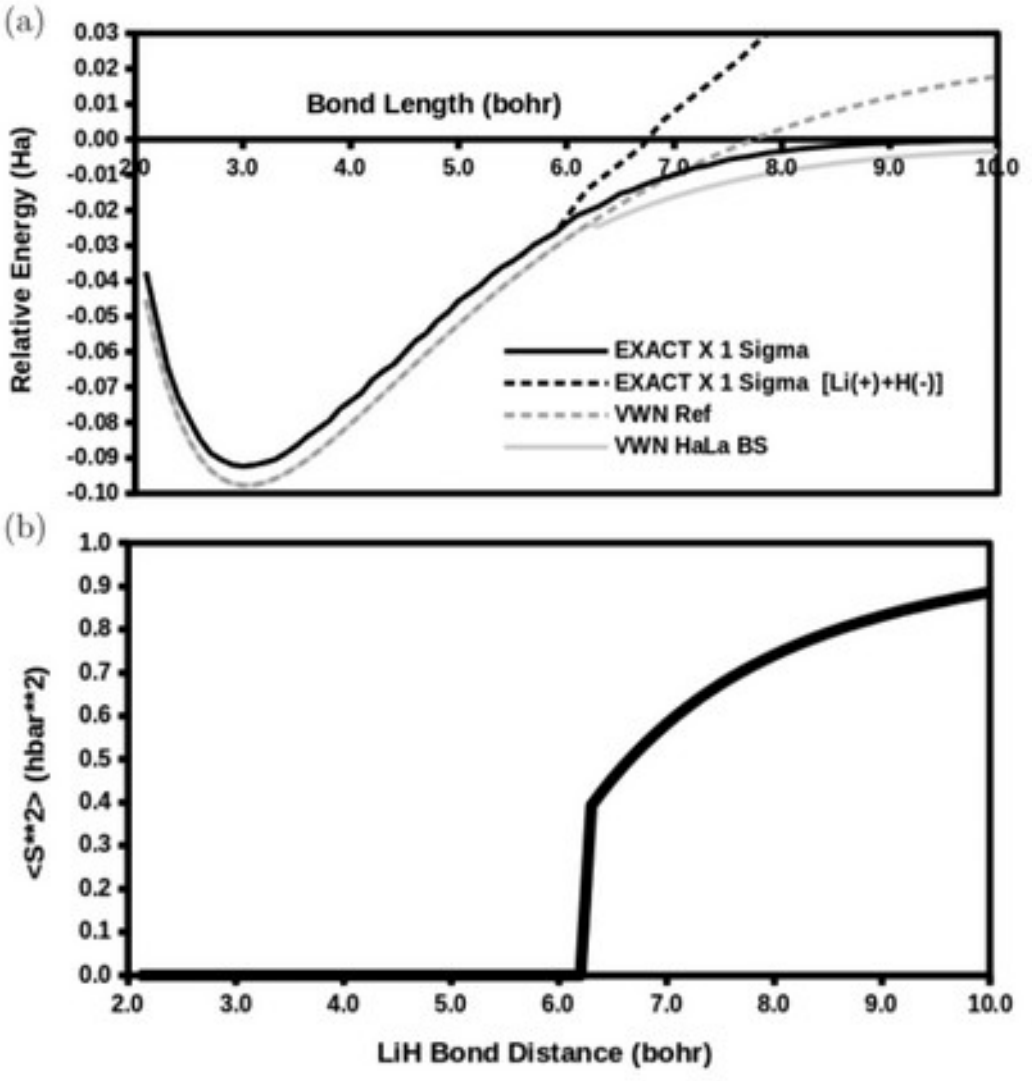


FIG. 14. Decomposition of the diagrammatic MSM-LDA CI wave function calculated with *unsymmetrized* matrix elements as a function of LiH bond length: Weight Phi0, $|H,\bar{H}|$; weight PhiS, $(1/\sqrt{2})(|H,\bar{L}| + |L,\bar{H}|)$; and weight PhiD, $|L,\bar{L}|$. The Phi0 and PhiS weights cross at about 4.9 bohr.



Why we need to include relaxation!

- **Focus on LiH.**
- **Use different optimal MOs for the ground-state, spin multiplets, and doubly-excited states.**
- **Experiment with the best references for calculating C and D.**
- **Include the CI overlap matrix as time allows.**

Unity in Diversity: Siamese crocodiles with one shared stomach.

(We think we are different, but really we are one.)