Energy and polarizability calculation of LiH using varational Monte Carlo

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Abstract

The purpose of this project is to estimate the energy, dipole moment (μ_z), and the dipole polarizability (α_{zz}) for LiH using variational Monte Carlo (VMC).

In VMC a trial function [ψ] guides the simulation. The closer the trial function is to the true one, the more accurate the results are. In our case the trial function was generated by taking a linear combination of determinants [Φ], which are constructed from the spin-up and spin-down molecular orbitals [ϕ^α, ϕ^β, respectively], linear combinations of atomic orbitals [χ]. The atomic orbitals are linear combinations of gaussian functions [γ].

The trial function is given as follows:

$$\psi = \textstyle\sum_i A_i \cdot \Phi_i$$

$$\Phi_i = \begin{vmatrix} \phi_l^\alpha(1) & \phi_m^\alpha(1) \\ \phi_l^\alpha(2) & \phi_m^\alpha(2) \end{vmatrix} \begin{vmatrix} \phi_n^\beta(3) & \phi_o^\beta(3) \\ \phi_n^\beta(4) & \phi_o^\beta(4) \end{vmatrix}$$

$$\phi_i = \textstyle\sum B_{ij} \cdot \chi_j$$
$$\chi_j = \textstyle\sum C_{ju} \cdot \gamma_u$$
$$\gamma_u = N x^a y^b z^c e^{-\zeta r^2}$$

where N is the normalization constant, and a,b,c, and ζ describe the atomic orbital.

The properties of interest were calculated for LiH as the number of determinants and the number of atomic orbitals in the trial function were varied. So far we have qualitatively but not yet quantitively reproduced the accepted values of LiH. We will improve on our calculations by performing more accurate sampling than variational Monte Carlo.

Suggested Readings

1 *Monte Carlo Methods in Ab Initio Quantum Chemistry*; Hammond, B.L.; Lester, Jr. W.A.; Reynolds, P.J.; World Scientific; Singapore, 1994.

2 *Quantum Monte Carlo: Origins, Development, Applications*; Anderson, J.B.; Oxford; New York, 2007.

3 Aspuru-Guzik, A.; Lester Jr., W.A. In *Handbook of Numberical Analysis: Computation Chemistry, Vol. 10*; Ciarlet, P.G., LeBris, C., Eds; North Holland; Amsterdam, 2003; p 485.