

COMMENTS

Comment on "Quantum Monte Carlo study of the dipole moment of CO" [J. Chem. Phys. 110, 11700 (1999)]

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In a recent paper Schautz and Flad¹ studied the dipole moment of CO using various first-principles computational methods. As part of this study they considered the applicability of the Hellmann–Feynman theorem within the fixed-node diffusion quantum Monte Carlo (DMC) method.^{2–4} The purpose of this comment is to point out that the conclusion reached by Schautz and Flad¹ regarding the applicability of the Hellmann–Feynman theorem within fixed-node DMC is incorrect.

In the DMC method stochastic evolution of the imaginary-time Schrödinger equation is used to project out the lowest energy many-electron wave function. Such projector methods suffer from a fermion sign problem in which the wave function decays towards the bosonic ground state. To enforce the fermion symmetry the fixed-node approximation^{5,6} is normally used. In a fixed-node DMC calculation the Schrödinger equation is solved separately in each nodal pocket with the boundary condition that the wave function in the α th pocket, ψ_α , is zero on the surface of the pocket. For simplicity we consider only ground-state wave functions which satisfy the tiling property^{7,8} that all nodal pockets are equivalent and related by the permutation symmetry. The pocket wave function is zero outside the pocket and has a discontinuous derivative at the surface of the pocket and, therefore, satisfies⁸

$$\hat{H}\psi_\alpha = E_D\psi_\alpha + g[\psi_\alpha] \delta(\mathbf{r} - \mathbf{r}_n[\psi_\alpha]), \quad (1)$$

where $\mathbf{r}_n[\psi_\alpha]$ is the surface of pocket α . The delta function term, which was neglected by Schautz and Flad,¹ arises from the action of the kinetic-energy operator on the discontinuity in the derivative of the wave function at the pocket surface. Operating on this equation with the antisymmetrizing operator, \hat{A} , gives

$$\hat{H}\Psi = E_D\Psi + h[\Psi] \delta(\mathbf{r} - \mathbf{r}_n[\Psi]), \quad (2)$$

where $\Psi = \hat{A}\psi_\alpha$ is the antisymmetric DMC wave function and $\mathbf{r}_n[\Psi]$ is the nodal surface of Ψ . The nodal surface is fixed by the choice of the trial wave function, Φ_T . The DMC energy may then be calculated from

$$E_D = \frac{\int \Phi_T \hat{H} \Psi \, d\mathbf{r}}{\int \Phi_T \Psi \, d\mathbf{r}}. \quad (3)$$

If the nodal surface of Φ_T is exact then Ψ has no gradient discontinuities on the nodal surface and $\hat{H}\Psi_0 = E_0\Psi_0$, where Ψ_0 and E_0 are the exact wave function and energy, but if the nodal surface is inexact then $h[\Psi]$ is nonzero and normally of order $\Psi - \Psi_0$. On substituting Eq. (2) into Eq. (3) we find that the nodal term, $h\delta$, does not contribute to the energy because Φ_T is zero on the nodal surface. However, the nodal term *can* contribute to derivatives of E_D . A simple way to see this is to note that the DMC energy can also be evaluated as the expectation value with the fixed-node DMC wave function

$$E_D = \frac{\int \Psi \hat{H} \Psi \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}}. \quad (4)$$

The derivative with respect to a parameter, λ , is

$$\begin{aligned} \frac{\partial E_D}{\partial \lambda} &= \frac{\int \Psi (\partial \hat{H} / \partial \lambda) \Psi \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}} \\ &+ 2 \frac{\int (\partial \Psi / \partial \lambda) \hat{H} \Psi \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}} - 2E_D \frac{\int \Psi (\partial \Psi / \partial \lambda) \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}}, \end{aligned} \quad (5)$$

and using Eq. (2) we obtain

$$\frac{\partial E_D}{\partial \lambda} = \frac{\int \Psi (\partial \hat{H} / \partial \lambda) \Psi \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}} + 2 \frac{\int (\partial \Psi / \partial \lambda) h \delta \, d\mathbf{r}}{\int \Psi \Psi \, d\mathbf{r}}, \quad (6)$$

which is the Hellmann–Feynman expression with an additional nodal term. While $h\delta$ is determined by the nodes of Ψ (or equivalently those of Φ_T), $\partial \Psi / \partial \lambda$ depends on how we choose the nodes to vary with λ . We, therefore, expect the nodal term in Eq. (6) to be nonzero in general. If we choose the nodes to be independent of λ then $\partial \Psi / \partial \lambda = 0$ on the nodal surface and the contribution from the nodal term is zero. In this case the Hellmann–Feynman theorem holds, as correctly stated by Schautz and Flad.¹ However, if the nodes of the trial wave function vary with λ then the nodal term will normally be nonzero and the Hellmann–Feynman ex-

pression does not give the exact derivative of the DMC energy of Eqs. (3) and (4), in contradiction to Schautz and Flad.¹

We conclude that Schautz and Flad are correct in stating that the Hellmann–Feynman expression evaluated with the fixed-node DMC wave function is equal to the derivative of the fixed-node DMC energy with respect to a parameter λ *if the nodes are independent of λ* , but this does not hold in general if the nodal surface depends on λ .

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