In a recent paper Schautz and Flad\(^1\) 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 Flad\(^1\) 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 lowest energy many-electron wave function. Such projection methods suffer from a fermion sign problem in which the lowest energy many-electron 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 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, satisfies

\[
\hat{H} \psi_a = E_D \psi_a + g[\psi_a] \delta(r - r_a[\psi_a]), \tag{1}
\]

where \(r_a[\psi_a]\) is the surface of pocket \(a\). 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

\[
\hat{A} \hat{H} \psi_a = E_D \psi_a + h[\psi_a] \delta(r - r_a[\psi_a]), \tag{2}
\]

where \(\psi_a = \hat{A} \psi_a\) is the antisymmetric DMC wave function and \(r_a[\psi_a]\) is the nodal surface of \(\psi_a\). The nodal surface is fixed by the choice of the trial wave function, \(\Phi_T\). The DMC energy may then be calculated from

\[
E_D = \frac{\int \Phi_T \hat{H} \psi_a \, dr}{\int \Phi_T \psi_a \, dr}. \tag{3}
\]

If the nodal surface of \(\Phi_T\) is exact then \(\psi_a\) has no gradient discontinuities on the nodal surface and \(\hat{A} \hat{H} \psi_a = E_D \psi_a\), where \(\psi_a\) and \(E_D\) are the exact wave function and energy, but if the nodal surface is inexact then \(h[\psi_a]\) is nonzero and normally of order \(\psi_a - E_D\). On substituting Eq. (2) into Eq. (3) we find that the nodal term, \(h \delta\), does not contribute to the energy because \(\Phi_T\) 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

\[
E_D = \frac{\int \hat{A} \hat{H} \psi_a \, dr}{\int \psi_a \, dr}. \tag{4}
\]

The derivative with respect to a parameter, \(\lambda\), is

\[
\frac{\partial E_D}{\partial \lambda} = \frac{\int \partial \hat{H} / \partial \lambda \psi_a \, dr}{\int \psi_a \, dr} + 2 \frac{\int (\partial \psi / \partial \lambda) \hat{H} \psi_a \, dr}{\int \psi_a \, dr} - 2E_D \frac{\int (\partial \psi / \partial \lambda) \, dr}{\int \psi_a \, dr}, \tag{5}
\]

and using Eq. (2) we obtain

\[
\frac{\partial E_D}{\partial \lambda} = \frac{\int \partial \hat{H} / \partial \lambda \psi_a \, dr}{\int \psi_a \, dr} + 2 \frac{\int (\partial \psi / \partial \lambda) h \delta \, dr}{\int \psi_a \, dr}, \tag{6}
\]

which is the Hellmann–Feynman expression with an additional nodal term. While \(h \delta\) is determined by the nodes of \(\Psi\) (or equivalently those of \(\Phi_T\)), \(\partial \psi / \partial \lambda\) depends on how we choose the nodes to vary with \(\lambda\). We, therefore, expect the nodal term in Eq. (6) to be nonzero in general. If we choose the nodes to be independent of \(\lambda\) 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 \(\lambda\) 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.\textsuperscript{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 \( \lambda \) if the nodes are independent of \( \lambda \), but this does not hold in general if the nodal surface depends on \( \lambda \).

\textsuperscript{4}Present address: Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139-4307.