On nonadiabatic SCF calculations of molecular properties

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Abstract
We argue that the dynamic extended molecular orbital (DEMO) method may be less accurate
than expected because the motion of the centre of mass was not properly removed prior to the
SCF calculation. Under such conditions the virial theorem is a misleading indication of the
accuracy of the wavefunction.

1. Introduction

The first step in any quantum-mechanical treatment of atomic and molecular systems is the separation of the motion of the centre of mass. The nonrelativistic Hamiltonian operator with only Coulomb interactions between the constituent particles for such systems is of the form $\hat{H}_T = \hat{T} + V$, where $\hat{T}$ is the total kinetic-energy operator and V is the sum of all the Coulomb interactions between the charged particles. By means of a straightforward linear combination of variables one rewrites the kinetic-energy operator as $\hat{T} = \hat{T}_{CM} + \hat{T}_{rel}$, where $\hat{T}_{CM}$ and $\hat{T}_{rel}$ are the operators for the kinetic energies of the centre of mass and relative motion, respectively. Then one solves the Schrödinger equation for the internal Hamiltonian $\hat{H} = \hat{T}_{rel} + V$ [1–3].

It is well known that the eigenfunctions of $\hat{H}_T$ are not square integrable because of the free motion of the centre of mass. For this reason, it is at first sight striking that Tachikawa *et al* [4, 5] carried out their dynamic extended molecular orbital (DEMO) method on the total Hamiltonian operator $\hat{H}_T$. A question therefore arises: how much did this omission affect the results of their nonadiabatic calculation of molecular properties? In this paper we will try to answer it.

In section 2 we analyse the results of Tachikawa *et al* [4, 5] and compare them with other nonadiabatic calculations [2, 3]. In section 3 we carry out simple illustrative calculations on a toy model. Finally, in section 4 we summarize our results and draw conclusions.

2. Analysis of the DEMO results

Suppose that we try to approximate the energy of the system by minimization of the variational energy $W = \langle \hat{H}_T \rangle =$ $\langle \varphi | \hat{H}_T | \varphi \rangle / \langle \varphi | \varphi \rangle$ as in the DEMO method of Tachikawa *et al* [4, 5]. If the trial function φ depends only on translation-invariant coordinates, then $W = W_{rel} = \langle \hat{H} \rangle$ because $\langle \hat{T}_{CM} \rangle = 0$. However, if φ depends on the coordinates of the particles in the laboratory-fixed set of axes, as in the case of the SCF wavefunction used by Tachikawa *et al* (see, for example, equations (10) and (7) in [4] and [5], respectively), then $W = \langle \hat{T}_{CM} \rangle + \langle \hat{H} \rangle > W_{rel}$. From the variational principle we know that $W_{rel} \geqslant E_0$, where E_0 is the exact ground-state energy of the atomic or molecular system. Therefore, the use of $\hat{H}_T$ (instead of $\hat{H}$) and a laboratory-fixed set of axes for the electronic and nuclear coordinates in φ will result in an even larger estimation of the molecular energy.

It is well known that the SCF wavefunction satisfies the virial theorem [5, 6] $2\langle \hat{T} \rangle = -\langle V \rangle$, but in the DEMO approach we have a wrong relation because $\langle \hat{T} \rangle = \langle \hat{T}_{CM} \rangle + \langle \hat{T}_{rel} \rangle > \langle \hat{T}_{rel} \rangle$. Therefore, under such conditions the virial theorem may be a misleading indication of the quality of the wavefunction.

Table 1 shows the ground-state energies of some diatomic molecules calculated with the internal Hamiltonian operator [2, 3] and also the corresponding DEMO results of Tachikawa and Osamura [5] who did not remove the motion of the centre of mass. As expected the uncorrelated SCF energies are greater than those in which particle correlation is explicitly taken into account [2, 3]. In addition to it, we also expect the energy difference $\Delta W = W^{TO} - W^{KA}$ (where TO and KA stand for Tachikawa and Osamura [5] and Kinghorn and Adamowicz [3], respectively) to depend on the expectation value $\langle \hat{T}_{CM} \rangle$ that should decrease as the molecular mass increases. In fact, the third column of table 1 shows this trend as expected from the fact that $\langle \hat{T}_{CM} \rangle$ is inversely proportional to the total molecular mass. If this argument were correct, then ΔW would exhibit
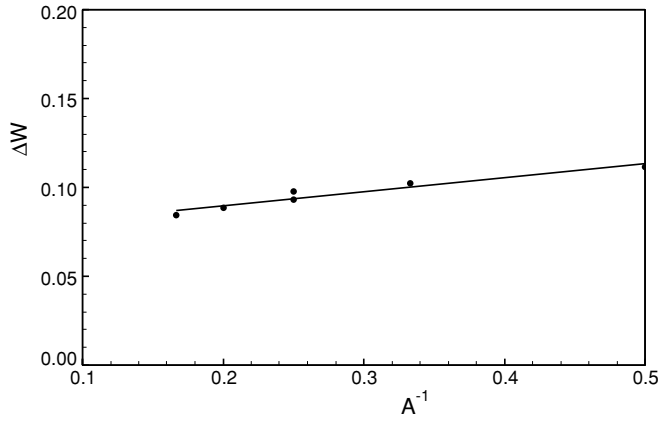
Figure 1. ΔW versus A^{-1} for the H_2 isotopic series shown in table 1.

Table 1. Nonadiabatic energies of some diatomic molecules.

Ref.	W	ΔW
	H_2	
KA00	$-1.164\,025\,0232$	$0.111\,654$
TO00	$-1.052\,371$	
	HD	
KW66	$-1.165\,4555$	
KA00	$-1.165\,471\,8927$	$0.102\,116$
TO00	$-1.063\,356$	
	HT	
KA00	$-1.166\,002\,0061$	$0.098\,7868$
TO00	$-1.068\,382$	
	D_2	
KA00	$-1.167\,168\,8033$	$0.091\,8650$
TO00	$-1.074\,137$	
	DT	
KA00	$-1.167\,819\,6334$	$0.088\,5406$
TO00	$-1.079\,279$	
	T_2	
KA00	$-1.168\,535\,6688$	$0.084\,4127$
TO00	$-1.084\,123$	

an almost linear relation with the inverse of the mass number A. Figure 1 shows that this is in fact the case for the values of the energy difference shown in table 1.

In the following section we test the arguments above on an anharmonic oscillator that leads to a nontrivial Schrödinger equation that we can solve accurately.

3. Toy model

In order to illustrate (and in some way corroborate) the arguments above we consider the simple but nontrivial anharmonic oscillator:

$$\hat{H}_T = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + k(x_1 - x_2)^4. \tag{1}$$

In terms of the relative $x = x_1 - x_2$ and centre of mass $X = (m_1 x_1 + m_2 x_2)/M$ coordinates, where $M = m_1 + m_2$, we have

$$\hat{H}_T = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + kx^4 \tag{2}$$

where $m = m_1 m_2/M$ is the reduced mass. The first and second terms on the right-hand side of this equation are simple examples of the operators $\hat{T}_{CM}$ and $\hat{T}_{rel}$, respectively, mentioned above in section 2. This toy model may seem to be rather too unrealistic at first sight but it exhibits some of the features of more complex problems that we need for present discussion. First, it is separable into centre of mass and relative degrees of freedom. Second, we can device a simple variational function of coordinates x_1 and x_2 defined in the laboratory-fixed set of axes as well as a function of the more convenient relative variable x. Third, we can calculate the eigenvalues of the relative Hamiltonian operator quite accurately, which are useful for comparison.

To simplify the calculation we resort to the dimensionless coordinates $q_i = x_i/L$, where $L = [\hbar^2/(m_1 k)]^{1/6}$, and the total dimensionless Hamiltonian operator

$$\hat{H}_{Td} = \frac{m_1 L^2}{\hbar^2}\hat{H}_T = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{\beta}{2}\frac{\partial^2}{\partial q_2^2} + (q_1 - q_2)^4 \tag{3}$$

where $\beta = m_1/m_2$. Analogously, the dimensionless relative Hamiltonian operator is given by

$$\hat{H}_d = -\frac{\beta + 1}{2}\frac{\partial^2}{\partial q^2} + q^4 \tag{4}$$

where $q = q_1 - q_2$ is the translation-invariant coordinate.

We first consider the trial function

$$\varphi_r(a, q) = \exp(-aq^2) \tag{5}$$

where a is a variational parameter, and apply the variational method to the total dimensionless Hamiltonian operator (3). Note that the trial function (5) depends only on the relative coordinate q so that $\langle \hat{T}_{CM} \rangle = 0$ and $\langle \hat{H}_{Td} \rangle = \langle \hat{H}_d \rangle$. The calculation is straightforward and we obtain

$$W_r = \frac{3 \cdot 6^{1/3}(\beta + 1)^{2/3}}{8}. \tag{6}$$

Obviously, the optimized trial function (5) satisfies the virial theorem

$$\langle \hat{T} \rangle = \langle \hat{T}_{rel} \rangle = 2\langle \hat{V} \rangle = \frac{6^{1/3}(\beta + 1)^{2/3}}{4}. \tag{7}$$

In order to simulate an SCF function of the laboratory-fixed coordinates we consider

$$\varphi_{nr}(a, b, q_1, q_2) = \exp\left(-aq_1^2 - bq_2^2\right). \tag{8}$$

The calculation is also straightforward and we obtain

$$W_{nr} = \frac{3 \cdot 6^{1/3}(\sqrt{\beta} + 1)^2}{[8(\sqrt{\beta} + 1)^{2/3}]} > W_r.$$

The optimized trial function (8) also satisfies the virial theorem $\langle \hat{T} \rangle = 2\langle \hat{V} \rangle$, but in this case $\langle \hat{T} \rangle > \langle \hat{T}_{rel} \rangle$ as discussed above in section 2.
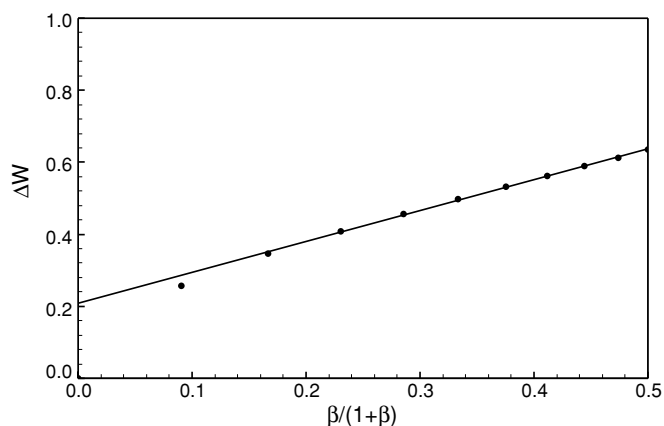
Figure 2 shows W_r, W_{nr} and an accurate numerical calculation of the ground-state energy of the dimensionless relative Hamiltonian operator (4) for $0 < \beta < 1$. We clearly
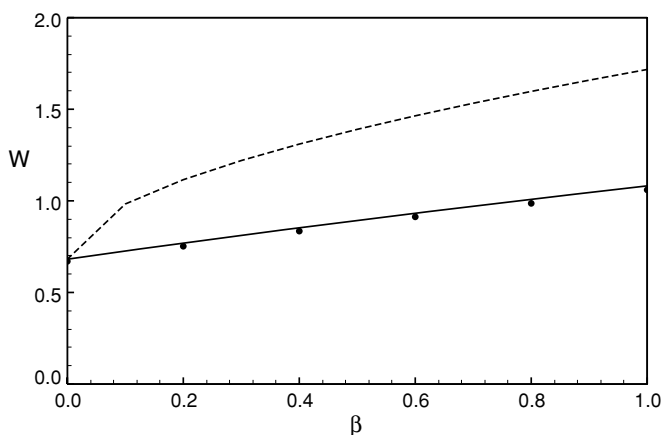
Figure 2. Ground-state energy of the anharmonic oscillator calculated with the variational function of the relative (solid line) and laboratory-fixed (dashed line) coordinates and the accurate numerical results (circles).

Figure 3. ΔW versus $\beta/(1 + \beta)$ for the ground state of the anharmonic oscillator.

appreciate the advantage of using a trial wavefunction of internal coordinates. The trial function (8) yields considerably poorer results in spite of having one more adjustable variational parameter. We do not claim that the error in the DEMO calculation of molecular energies [4, 5] is as large as the one exhibited by the present anharmonic oscillator, but this simple model shows (at least) two aspects of the problem. First, that the energy calculated by trial functions of the laboratory-fixed coordinates may be considerably greater than those coming from the use of relative coordinates if we do not remove the motion of the centre of mass properly. And, second, that the virial theorem is not a reliable indication of the quality of the wavefunction if it is not based on the relative kinetic energy.

We can carry out another numerical experiment with the toy model. The total mass in units of m_1 is $M/m_1 = (1+\beta)/\beta$. Figure 3 shows that $\Delta W = W_{nr} - W_r$ depends almost linearly on $\beta/(1 + \beta)$ (at least for some values of β) as suggested in section 2 for the actual molecular energies and illustrated in figure 2. We appreciate that the toy model gives us another hint on the difference between the actual molecular energies calculated by Kinghorn and Adamowicz [3] and Tachikawa and Osamura [5].

4. Conclusions

If we do not properly separate the motion of the centre of mass in a calculation of atomic or molecular energies, we expect inaccurate results unless the approximate trial function depends only on internal, translation-free coordinates. Otherwise, the effect of the kinetic energy of the centre of mass will be a too large estimate of the energy. Under such conditions the virial theorem will result in a misleading indication of a supposedly accurate wavefunction. These arguments apply to the case in which all the particles are allowed to move [5] and may not be valid when some heavy particles [4] (or all the nuclei [5]) are considered as mere point charges (a sort of clamped nucleus approximation).

References

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