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Direct determination of the density matrix using the density equation: potential energy curves of HF, CH_4, BH_3, NH_3, and H_2O

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Abstract

The density equation (DE) method was utilized for calculations of the potential energy curves of the molecules HF, CH_4, BH_3, NH_3, and H_2O. The equilibrium geometries and the vibrational force constants of these molecules were determined by the DE method without any use of the wavefunction. The calculated values are in close agreement with the results of the symmetry-adapted cluster (SAC) and full-CI methods. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, a revival of interest has been invoked on the direct determination of the density matrix (DM) without any use of the wavefunction [1–12]. The density matrix approach is straightforward in comparison with the wavefunction approach, since all the elemental physical quantities can be calculated using second-order density matrices (2-DMs). The basic equation for the DMs exists in an explicit form [1], in contrast to Hohenberg–Kohn's existing theorem [13] in the density functional approach [14]. In 1976, Nakatsuji derived a basic equation, called density equation (DE), for a direct determination of the DM [1]. Recently, time-dependent DE and the perturbation theory for both time-independent and time-dependent DEs were published [2]. He showed

that the DE is *equivalent* to the Schrödinger equation (by the *necessary and sufficient* condition) in the domain of the N-representable DMs. Unfortunately, the N-representability condition on the DM is still not completely known [15], and under such a situation, the nth-order DE, containing the nth, $(n + 1)$th, and $(n + 2)$th-order DMs is formally insoluble, for the number of the unknown variables exceeds the number of conditions.

Valdemoro and co-workers reported an interesting approach for solving the density equation [6–10]. (They referred to the DE as the contracted Schrödinger equation, but this naming does not well represent the *sufficiency* nature of the DE, which is a primary feature of the DE.) They suggested a decoupling approximation of higher-order reduced density matrices (RDMs) in terms of the lower-order ones based on the fermion's anticommutation relation. We call this approximation the IPH approximation (the

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approximation identifying independently the particle and hole parts separately). Nakatsuji and Yasuda proposed a more accurate decoupling approximation on the basis of the Green's function method [3,4]. It was called the DE2 method since the approximation is correct essentially to the second order in the correlation perturbation. The method was applied to the calculations of the second-order RDMs of Be, Ne, H_2O, NH_3, H_3O^+, CH_4, BH_4^-, NH_4^+, CH_3F, HF, N_2, CO, C_2H_2, CH_3OH, CH_3NH_2, and C_2H_6 [3,4]. The RDMs of the molecules were determined directly, for the first time, and without any use of wavefunctions. Recently, the method has been reformulated for spin-dependent DMs and has been applied to some open-shell systems [5]. Mazziotti [11,12] recently reported a fresh reformulation of the DE method and applied it to the Lipkin model.

In this Letter, the DE2 method is applied to the calculations of the potential energy curves of some small molecules. We want to calculate their equilibrium geometries and force constants by the DE method.

2. Computational method

The DE2 method proposed in previous papers [3,4] is applied to the calculations of the potential curves of HF, CH_4, BH_3, NH_3, and H_2O. The calculational procedure was discussed in detail elsewhere [4]. We did not include the term given by Eq. (2.24) of Ref. [4]. The multidimensional nonlinear equation was solved by Newton's method. The Hermiticity and the symmetry properties of the 2-RDM were imposed in solving the DE.

The valence double-zeta basis, [3s2p/2s] set [16,17], was used for HF and the minimal STO-6G basis [18] was used for CH_4, BH_3, NH_3, and H_2O. The potential energy curves of HF, CH_4, BH_3, and NH_3 were calculated for the totally-symmetric stretching mode. The potential energy surface of H_2O was calculated along the three normal modes around the equilibrium geometry. The spectroscopic constants of the potential curves were calculated numerically. The full-CI and symmetry-adapted-cluster (SAC) [19] methods were performed, at the same time, to examine the accuracy of the present DE2 results. The HONDO8 program [20] was used for the

Hartree–Fock and full-CI calculations and the SAC-CI96 program [21] for SAC calculations.

In all calculations, the 1s orbitals of the first-row atoms were frozen as cores. This was effective to get a good convergence in the present algorithm of solving the DE. When these 1s orbitals were included, the breakdown of the *N*-representability of the 1-RDM occurred even at the geometries relatively close to the equilibrium geometry. The origin of this non-convergence is not clear, but we have observed that the occupation number of the 1s orbitals slightly exceeds two, when the molecular geometry is apart from the equilibrium geometry. By adopting the 1s orbitals as a frozen core, the present DE2 calculations have converged in wide regions around the equilibrium geometry.

3. Stretching potential for HF, CH_4, BH_3, and NH_3

Fig. 1a shows a comparison of the ground-state potential energy curves of HF molecule calculated by the Hartree–Fock, DE2, SAC, and full-CI methods in the nuclear distance of 0.8–1.2 Å. The DE2 method well reproduces the full-CI curve, showing that the DE2 method includes electron correlations accurately: the errors range from 4.1 to 9.2% in these internuclear distances. The deviations from the full-CI are larger at the large internuclear distance, while a weight of the Hartree–Fock configuration is almost constant, 0.96–0.95, in the distance of 0.8–1.2 Å. The SAC almost reproduces the full-CI curve: the deviations are within 1.8 mhartree.

The potential curves for the totally-symmetric stretching mode of CH_4 are shown in Fig. 1b. Again, the DE2 method simulates well the full-CI curve: for CH_4, the errors in the correlation energy are 3.3–13.1% in the range of $R_{C-H} = 0.95$–1.40 Å, where the weight of the Hartree–Fock configuration changes from 0.97 to 0.88, the last figure being very small. Since the present DE2 method is based on the perturbation expansion by the Green's function method [3,4], a better agreement is obtained at a shorter internuclear distance where the Hartree–Fock approximation becomes better. The SAC curve is almost superposed with the full-CI one. The DE2 method is correct to the second order in the correlation perturbation, but still is a subject of improve-
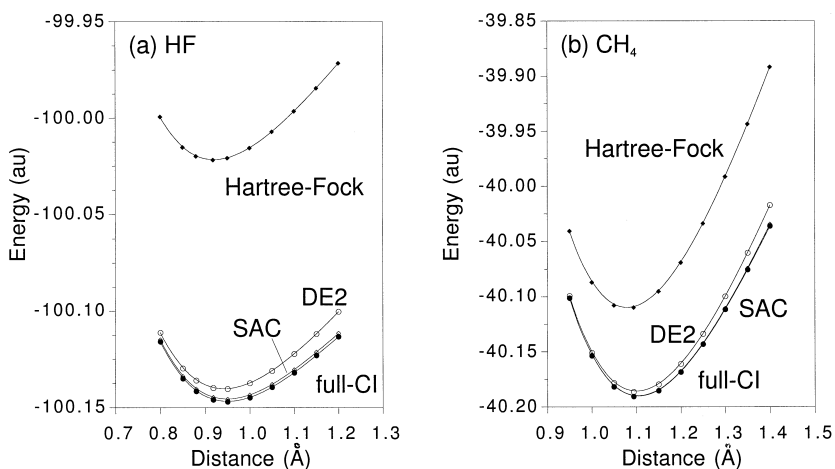
Fig. 1. Potential energy curves of (a) HF and (b) CH_4, calculated by the Hartree–Fock, DE2, SAC, and full-CI methods.

ment and at this moment, it is more expensive than a wavefunction approach like SAC.

The potential curves of BH_3 and NH_3 are depicted in Fig. 2 for the totally-symmetric stretching mode. The stretching potential of BH_3 was obtained by restricting the planer structure of D_{3h}, while for NH_3 the geometry was optimized along the mode by each method. The weight of the Hartree–Fock configuration is 0.98–0.93 for $R_{B-H} = 1.0$–1.45 Å of BH_3 and 0.97–0.93 for $R_{N-H} = 0.948$–1.185 Å of NH_3. The DE2 method describes 96.7–89.0% of the electron correlations of BH_3 and 92.6–89.8% for NH_3, though the geometry of NH_3 is different for each method.

The spectroscopic constants were numerically evaluated from the potential energy curves of the Hartree–Fock, DE2, SAC, and full-CI methods. The equilibrium distance R_e and the harmonic vibrational frequency ω_e are summarized in Table 1 for HF, CH_4, and BH_3 and the optimized geometry and the harmonic frequency of NH_3 are given in Table 2. The equilibrium geometry calculated by the DE2 method is very close to the full-CI result for all the molecules, and the harmonic vibrational frequency of
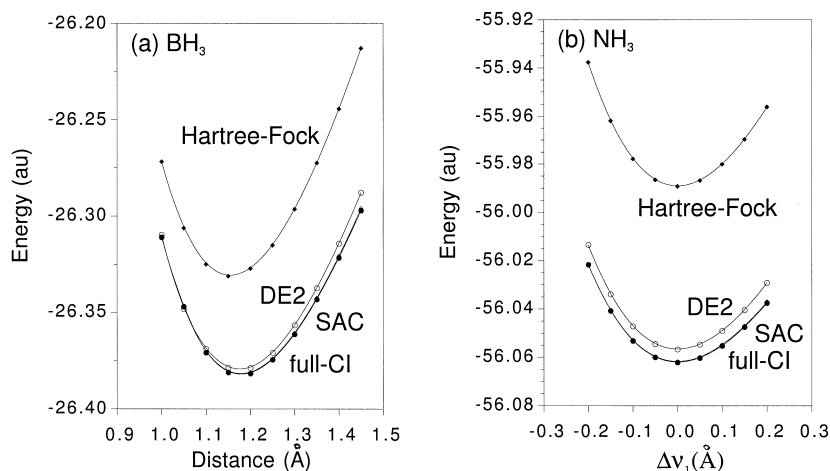

Fig. 2. Potential energy curves for the totally-symmetric stretching modes of (a) BH_3 and (b) NH_3, calculated by the Hartree–Fock, DE2, SAC, and full-CI methods.

Table 1
The equilibrium length R_e and totally-symmetric harmonic vibrational frequency ω_e calculated for HF, CH_4, and BH_3

	R_e (Å)	ω_e (cm^{-1})
HF[a]:		
Hartree–Fock	0.9195	4233
DE2	0.9416	3969
SAC	0.9487	3826
Full-CI	0.9495	3808
CH_4[b]:		
Hartree–Fock	1.0783	3535
DE2	1.0998	3306
SAC	1.1035	3245
Full-CI	1.1038	3240
BH_3:		
Hartree–Fock	1.1539	3114
DE2	1.1743	2929
SAC	1.1774	2879
Full-CI	1.1778	2884

[a]Experimental values are $R_e = 0.9168$ Å and $\omega_e = 4138$ cm^{-1} [22].
[b]Experimental values are $R_e = 1.0936$ Å [23] and $\omega_e = 2915$ cm^{-1} [24].

the DE2 method is much closer to the full-CI result than to the Hartree–Fock result. The SAC and full-CI results are almost the same.

It is important to examine not only the energy but also the details of the density. Fig. 3 shows the dipole moment of HF along the internuclear distance calculated by the Hartree–Fock, DE2, and full-CI

Table 2
Optimized geometry and vibrational frequency of the totally symmetric stretching mode of NH_3

	Hartree–Fock	DE2	SAC	Full-CI
Optimized geometry[a]:				
r_{NH} (Å)	1.0281	1.0580	1.0662	1.0664
θ_{HNH} (°)	104.46	101.07	100.28	100.29
Vibrational frequency[b]:				
$\nu_1(a_1)$ (cm^{-1})	3832	3496	3358	3350

[a]Experimental values are $r_{NH} = 1.0116$ Å and $\theta_{HNH} = 106.68°$ [23].
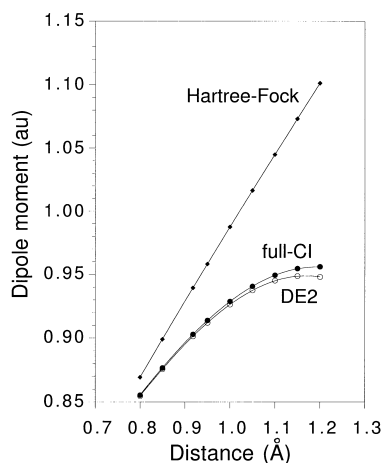[b]Experimental value is $\nu_1(a_1) = 3336$ cm^{-1} [24].

Fig. 3. Dipole moment vs. internuclear distance of HF calculated by the Hartree–Fock, DE2, and full-CI methods.

methods. The DE2 method reproduces well the full-CI result, which is reasonable since the DE2 method directly calculates the density matrix.

In the present DE2 calculation, the *N*-representability condition for the 1-RDM was satisfied for all the calculated geometries shown here: the eigenvalues of the 1-RDM, i.e. the occupation numbers, were all positive and less than two. As for the 2-RDM, the P, Q, and G conditions [3,4] for the *N*-representability were examined. Fig. 4 shows the lowest value and the sums of the negative eigenvalues of the P, Q, and G matrix of CH_4 along the internuclear distances shown in Fig. 1b. These values should be
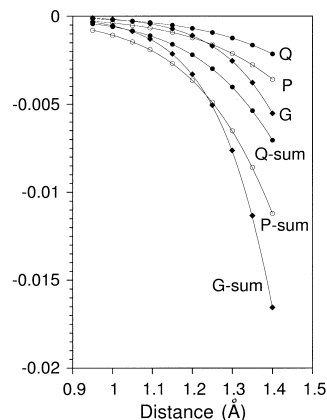

Fig. 4. Lowest values and the sums of the negative eigenvalues of the P, Q, and G matrices along the totally-symmetric vibrational mode of CH_4.

non-negative for the *N*-representative 2-RDM, but the lowest values are slightly negative from -1×10^{-4} at $R = 0.95$ Å to -6×10^{-3} at $R = 1.4$ Å. It should be noted that only 3 to 7 eigenvalues are negative out of the 336 independent variables and the sums of the negative values range from -3×10^{-4} to -1.6×10^{-2}. The calculated 2-RDM are not completely *N*-representable, but the deviation seems to be small. These conditions are satisfied better at shorter internuclear distances, as expected from the weight of the Hartree–Fock configuration.

We note here that at larger internuclear distances than those shown in this Letter, where the Hartree–Fock approximation becomes worse, the DE2 equation was rather unstable and sometimes failed to converge. When we examine the occupation numbers of the 1-RDM at such a geometry, some of them were negative showing that the *N*-representability condition was broken. This behavior of the DE implies that it is stable only for the *N*-representable or almost *N*-representable DMs.

4. Full vibrational potential of H_2O

Finally, the DE2 method was used to calculate the potential energy surface of the ground state of H_2O along the normal modes, $v_1(a_1)$, $v_2(a_1)$, and $v_3(b_1)$, totally-symmetric stretching, bending, and anti-symmetric stretching modes, respectively. Fig. 5 com-

Table 3
Optimized geometry and vibrational frequencies (cm^{-1}) for the $\nu_1(a_1)$, $\nu_2(a_1)$, and $\nu_3(b_2)$ modes of H_2O

	Hartree–Fock	DE2	SAC	Full-CI
Optimized geometry[a]:				
r_{OH} (Å)	0.9862	1.0146	1.0262	1.0264
θ_{HOH} (°)	100.01	97.47	96.68	96.68
Vibrational frequency[b]:				
$\nu_1(a_1)$	4102	3761	3515	3512
$\nu_2(a_1)$	2161	2078	2031	2027
$\nu_3(b_2)$	4352	4001	3758	3756

[a]Experimental values are $r_{OH} = 0.9575$ Å and $\theta_{HOH} = 104.51°$ [23].
[b]Experimental values are $\nu_1(a_1) = 3657$ cm^{-1}, $\nu_2(a_1) = 1595$ cm^{-1}, and $\nu_3(b_2) = 3756$ cm^{-1} [24].

pares the potential energy curves along these three modes around the equilibrium geometry determined by each method. The error in the electron correlation energy is relatively large for H_2O in comparison with other molecules. The errors were from 10.0 to 15.9% in the geometries examined here, although the weight of the Hartree–Fock configuration was as large as 0.95–0.97. The vibrational analysis was performed for these three modes and the results are given in Table 3 together with the optimized geometry. The DE2 method well reproduces the equilibrium geometry. The vibrational frequencies calcu-
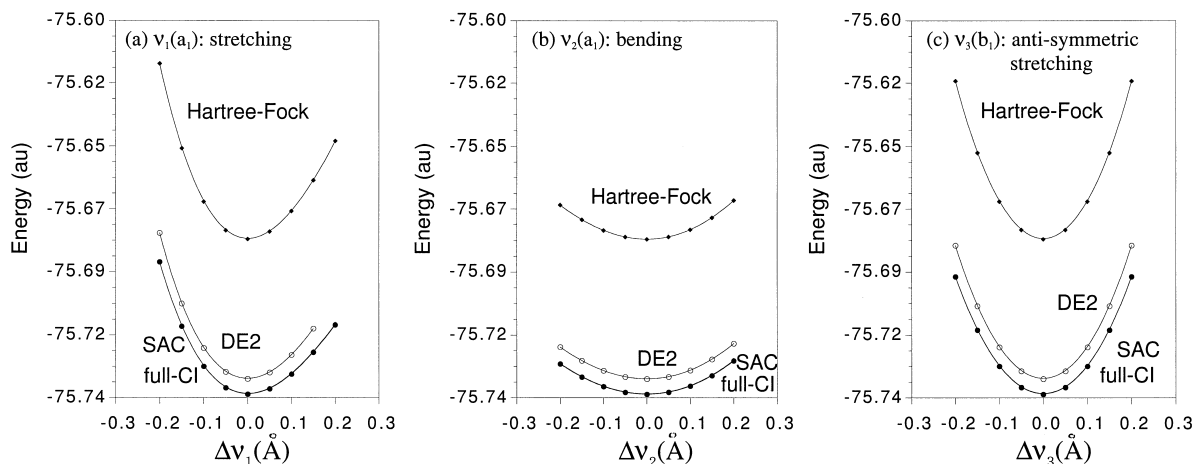

Fig. 5. Potential energy curves of H_2O for: (a) $\nu_1(a_1)$; (b) $\nu_2(a_1)$; and (c) $\nu_3(b_1)$ modes, calculated by the Hartree–Fock, DE2, SAC, and full-CI methods. Each curve is around the equilibrium geometry determined by each method.

lated by the DE2 method are closer to the full-CI values than to the Hartree–Fock ones.

5. Conclusions

The density equation method has been applied successfully, for the first time, to the calculation of the potential energy curves, equilibrium geometries, and vibrational force constants of molecules without using the wavefunctions. The results for HF, CH_4, BH_3, NH_3, and H_2O reproduced well the SAC and full-CI results. It was effective in the present algorithm to adopt the 1s orbital of the first-row atoms as frozen core. The resultant density matrices were almost N-representable, in the region reported in this Letter.

A note may be necessary about the Hartree–Fock method. When we introduce the independent particle approximation, we can derive the Hartree–Fock equation from the density equation as shown in Ref. [1]. In other words, the Hartree–Fock equation is a kind of density equation. We used the Hartree–Fock orbital which is obtained by diagonalizing the first-order density matrix, as reference functions in the second-quantized formulation. So, we never used any wavefunction.

Acknowledgements

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