Comparison of Hartree–Fock and Kohn–Sham Determinants as Wave Functions

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ABSTRACT: Kohn–Sham (KS) and Hartree–Fock (HF) determinants were used as the true many-body wave functions for calculations of molecular energies, vibrational frequencies, and excited electronic states. The results justified common practice, encountered in the sum over states theories, in which these two determinants are used as the first-order approximation of the wave function. However, a distinct behavior with respect to the second-order perturbation calculation was observed for the two cases. The Raleigh–Schrödinger perturbation theory, which is formally identical to the Levy–Görling formalism and analogous to the usual HF/Møller–Plesset approach, leads to rather discouraging results for the KS determinant. On the other hand, the rigid KS orbitals are more suitable for modeling of excited electronic states, which was indicated by the obtained transition energies for model molecules. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 8–16, 2000

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Introduction

The Kohn–Sham (KS) determinant is often used as an approximation to the molecular wave function in density functional theory (DFT) studies.[1] Also, the determinant may be taken as a reference point for further configuration interaction instead of the usual Hartree–Fock (HF) function.[2]

Although such approximations proved to be successful, they were done on an empirical basis. Indeed, there is no obvious physical meaning of the KS determinant, which was introduced originally as an arbitrary function for the construction of electron density. Thus, it appears important to evaluate the errors and other further aspects of this approximation as attempted in this study.

DFT analogues of electron wave functions are most frequently encountered in the modeling of excited electronic states. A crude approximation based on the rigid KS determinant proved to be equally or even more suitable than the HF ap-

proximation. This approach was used in sum over states (SOS) calculations of the nuclear magnetic resonance,[3,4] vibrational circular dichroism,[5,6] Raman optical activity,[7] and electronic circular dichroism spectra.[8] More detailed studies revealed a close relation between the KS orbital energies and experimental excitation energies. In particular, the difference of the KS eigenvalues was found to lie between triplet and singlet experimental excitation energies for exact functionals.[1] These studies suggest that KS one-electron and molecular excitation energies are closely related. The KS determinant can also be used as a starting point for the usual configuration interaction (CI) in advanced time-dependent DFT combined with the random phase approximation.[9]

The relation between the electron density and the wave function has been studied most extensively for atomic systems. The central symmetry of the nuclear field favored construction of optimal wave functions via constrained-search techniques.[10] Exploration of effective one-electron correlation-corrected potentials attracted attention as a tool for calculation of both the ground[11] and excited[12] state properties. Also, a close relation between HF, post-HF, and DFT densities stimulated many studies on this field for atomic,[12–14] and molecular[15] systems.

It was previously recognized that usual perturbation corrections can be applied directly to the KS determinant. Encouraging results were obtained for computation of excitation[1] or atomization[16] energies. Obviously, these corrections are necessary for resolution of singlet and triplet electron states.[1,4,8] The perturbation approach was elaborated in the work of Görling and Levy[17,18] who related the correction terms to the adiabatic theorem[19] and expanded the effective Hamiltonian in the Taylor series according to the electron–electron interaction term. Later Ernzenhof suggested that more sophisticated perturbation formulae may provide a faster convergence than the Görling–Levy formula (GL).[16] Nevertheless, the GL theory is adopted in this study for its simplicity. As shown below, general formalism based on the Raleigh–Schrödinger perturbation theory enables consistent treatment of the GL and the usual Møller–Plesset (MP) perturbation approach.[20,21] In the author's opinion, such a perturbation treatment reveals interesting properties of the KS determinant and enhances its comparison to the HF wave function.

In this work the HF and KS many-body wave functions are compared with respect to a wider range of molecular properties: molecular and atomization energies and vibrational and electronic excitation energy differences. Common DFT functionals and medium-sized basis sets are explored in order to obtain results that can be generalized for bigger molecules. Specific questions to be answered in this study include the errors caused by the KS and HF one-determinant approximation of the wave functions, the ability of the many-body perturbation theory to improve the results, the significance of the differences between KS and HF determinants for nonbenchmark calculations of single point energies and potential energy surfaces and how well the excited electronic states are represented with electronic configurations derived from frozen KS and HF determinants.

Basic equations are provided together with the perturbation formulae applicable for the KS determinant, because the DFT-perturbation approach is still rather rarely encountered in the literature. The basic properties of the KS determinant for three DFT functionals are documented on calculation of molecular, atomization, and vibrational energies of several small molecules. Finally, excitation energies for CH_2, formaldehyde, and acetone molecules are calculated using the one-determinant wave functions and compared to experimental values.

Theory

HF AND KS DETERMINANTS

The introductions of the HF and KS determinants had a revolutionary impact on quantum chemistry. In neither case can the determinant be directly used in the Schrödinger equation because of the self-interaction term. Nevertheless, consistency with the quantum mechanical formalism can be achieved with effective Hamiltonians containing simple scalar correction constants. Thus, instead of the exact many-body Hamiltonian,

$$H = \sum_i h_c(\mathbf{r}_i) + \sum_{j<i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

we define the HF Hamiltonian, H_{HF}, as

$$H_{HF} = \sum_i h_c(\mathbf{r}_i) + \sum_{j<i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \gamma_{HF}, \qquad (1)$$

where the one-electron "core" part $h_{c,i}(\mathbf{r}) = -(\Delta/2) + v(\mathbf{r})$, and the double-counting correction constant

$$\gamma_{HF} = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^{-1}} \, d\mathbf{r} \, d\mathbf{r}' + \frac{E_{HF,X}}{2}.$$

The sum runs over all electrons with position vectors $\mathbf{r}_i$, $v(\mathbf{r})$ is the nuclear potential, $\rho(\mathbf{r})$ is the electron density, and $E_{HF,X}$ is the usual HF exchange

energy. Atomic units are used. The determinant ϕ_{HF} corresponds to HF energy

$$E_{HF} = \langle\phi_{HF}|H_{HF}|\phi_{HF}\rangle = \langle\phi_{HF}|H|\phi_{HF}\rangle - \gamma_{HF}. \quad (2)$$

The KS equations[15, 22] can be analogously written, introducing a formal Hamiltonian

$$H_{KS} = \sum_i h_{KS}(\mathbf{r}_i) - \gamma_{KS}, \quad (3)$$

where h_{KS} is one-electron operator,

$$h_{KS}(\mathbf{r}) = -\frac{\Delta}{2} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{-1}}\,d\mathbf{r}' + v_{XC}(\mathbf{r}),$$

the constant

$$\gamma_{KS} = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{-1}}\,d\mathbf{r}\,d\mathbf{r}' + \int \rho(\mathbf{r})v_{XC}(\mathbf{r})\,d\mathbf{r} - E_{XC},$$

and v_{XC} and E_{XC} are the exchange-correlation potential and energy, respectively, $v_{XC}(\mathbf{r}) = \partial E_{XC}/\partial\rho(\mathbf{r})$. Thus, the KS determinant ϕ_{KS} also provides KS energy in the integral form

$$E_{KS} = \langle\phi_{KS}|H_{KS}|\phi_{KS}\rangle. \quad (4)$$

Obviously, in spite of the formalism similarities, neither ϕ_{KS} nor ϕ_{HF} is the true Schrödinger wave function. However, eq. (4) provides exact energy *in principle*, while eq. (2), which lacks the correlation energy, is intrinsically wrong.[23]

PERTURBATION CORRECTIONS

The differences between HF and KS determinants, especially the nonexistence of the Brillouin theorem[21] for the latter, are reflected in the corresponding perturbation calculations. Perturbation theory for DFT is often based on a Taylor expansion with respect to the electron–electron interaction term.[18] In this study the standard Rayleigh–Schrödinger perturbation theory is directly applied in order to emphasize the link to the HF and MP2 formalisms. As shown below, resulting second-order correction formulae are identical to those of Görling and Levi for the KS determinant and to the MP expressions for the HF approximation.

For an approximate Hamiltonian H_0 (either H_{KS} or H_{HF}) a perturbation potential may be introduced

$$V = H - H_0, \quad (5)$$

so that the usual perturbation expansion for the corrected energy of an eigenstate ϕ_0 of H_0 can be written as $E_0' = E_0 + E_0^{(1)} + E_0^{(2)} + \cdots$. For example, for the KS Hamiltonian and the ground state ($\phi_{KS} = \phi_0$)

$$E_0 + E_0^{(1)} = E_{KS} + \langle\phi_{KS}|V|\phi_{KS}\rangle = \langle\phi_{KS}|H|\phi_{KS}\rangle, \quad (6)$$

and

$$E_0^{(2)} = \sum_{q \neq \phi_{KS}} \frac{\langle q|V|\phi_{KS}\rangle^2}{E_{KS} - E_q}. \quad (7)$$

Usually a set of unoccupied molecular orbitals is calculated within a basis of atomic orbitals and the excited states $|q\rangle$ are obtained via changing of electron configuration in the ground state determinant.

Apparently, the unphysical self-interaction contribution also survives in the first-order perturbation term [eq. (6)]. Thus, it is convenient to directly subtract this constant in the Hamiltonian and define a new first-order perturbation energy for single-determinant wave functions as

$$E_{MP0} = \langle\phi_0|H_{HF}|\phi_0\rangle. \quad (8)$$

Index MP0 was appended in order to emphasize the link to the MP theory. Equation (7) can be divided into two terms corresponding to contributions from mono- and double-excited states ($\phi_{k\to j}, \phi_{k,k'\to j,j'}$), $E_0^{(2)} = \Delta E_{MP1} + \Delta E_{MP2}$, where

$$\Delta E_{MP1} = \sum_j \sum_k \frac{\left(\langle j|H|k\rangle + \sum_{k'}(jk||k'k')\right)^2}{\varepsilon_k - \varepsilon_j} \quad (9)$$

and

$$\Delta E_{MP2} = \sum_j \sum_{j'<j} \sum_k \sum_{k'<k} \frac{(jk||j'k')^2}{\varepsilon_k + \varepsilon_{k'} - \varepsilon_j - \varepsilon_{j'}}. \quad (10)$$

The electron-interaction term is defined in accordance with the usual notation,[13] $(ab||cd) = (ab|cd) - (ad|cb)$, and ε_j is the KS or HF one-electron energy of spin orbital j. The letters k and j are reserved for occupied and virtual spin orbitals, respectively. For the HF determinant $E_{MP0} = E_{HF}$ and $\Delta E_{MP1} = 0$ (Brillouin's theorem), while for the KS determinant all contributions are nontrivial.

HF ELECTRON DENSITY

It has been recognized that the self-consistency in KS equations may be omitted in cases when HF densities are directly used in DFT functionals. This approach can be encountered in the early stages of the DFT or in investigative studies,[15] because of the troublesome interpretation of such an approximation. Nevertheless, it is interesting to qualitatively compare this practice to the present work. The process of using HF density in KS equations will be referred to as "inverse" in order to emphasize its relation to the primary subject (using the KS determinant as the wave function). Thus, such an inverse (INV) energy [in a formal analogy to the "direct" substitution $E_{direct} = E_{MP0} = \langle\phi_{KS}|H_{HF}|\phi_{KS}\rangle$, see

eq. (8)] can be defined as

$$E_{INV} = \langle \phi_{HF} | H_{KS} | \phi_{HF} \rangle. \qquad (11)$$

Computation of E_{INV} can be easily done with Gaussian[24] and presumably with most of other quantum-chemical programs when the HF function is directly used for computation of the KS energy. As shown below, this procedure leads to comparable changes in energy because of the direct use of the KS determinant [eq. (8)] small overall error, and significant savings of computer time.

Results and Discussion

MOLECULAR ENERGIES

Energies of small systems calculated using the expressions above are collected in Table I. Molecular geometries were optimized at the MP2/6-311G** level of approximation using the Gaussian program.[24] The same basis set was used for the HF and KS determinants. Energies calculated at the QCISD(T)/aug-cc-pVTZ level were used as a reference point. Also, the QCISD(T)/6-311G** energies are given in order to estimate the error stemming from incompleteness of the basis set. However, no qualitative difference of the results under variation of the basis set size was observed. Three common DFT functionals were explored: the SVWN (LDA, LSDA) approximation,[10] the B3LYP hybrid functional,[25, 26] and the BPW91 combination of functionals,[25, 27] as implemented in Gaussian.

For all systems the HF/MP0 energies are lower than the KS/MP0 values, which is an obvious result of the variation principle. (Note that negative signs are skipped for energies in Table I.) Rather surprisingly, the KS determinants of the three distinct functionals behave quite similarly. For example, for the H_2O molecule the SVWN, BPW91, and B3LYP functionals yield energies (KS/KS) of 76.0812, 76.4398, and 76.4482 hartrees, respectively (i.e., within a dispersion of about 0.5%). However, the KS/MP0 expression gives 76.0338, 76.0378, and 76.0394 hartrees (i.e., a dispersion of about 0.007%). The KS/MP0 values are also very close to the HF limit (76.0463 for water), typically differing behind the second decimal point. Rather surprisingly, no qualitatively different behavior between the closed-shell and high-spin systems (^3C, ^3O, ^4N) can be observed.

The MP1 correction for the DFT values leads to energies almost identical to the HF limit and even slightly closer to the reference calculation (cf.

the average deviations a at the bottom of Table I). However, given the overall error and the additional computational cost connected with enumeration of eq. (9), little benefit of the MP1 correction can be expected in the usual computations of molecular energies. This is a rather unfortunate consequence of the similarity between HF and KS determinants, because the MP1 correction can still be computed with significantly smaller effort than the MP2 expression.

On the other hand, the MP2 correction significantly improves the agreement with the reference calculation, again regardless of the functional used. Typically, the KS/MP2 value is also better than or comparable to the sole KS/KS energy (compare the deviations of 0.141 and 0.072 for the B3LYP functional). This is in agreement with the generally accepted opinion that modern DFT functionals provide results of approximately the HF/MP2 quality. Apparently only the older SVWN approximation leads to an overall error comparable to the HF theory (cf. $a = -0.360$). The HF/MP2 values are generally closer to the reference calculation than the KS/MP2 energies, the latter significantly overestimate the correlation correction. Thus, the MP2 perturbation calculation with the KS determinant cannot be generally recommended.

Energies obtained by the inverse process are listed for the B3LYP functional only. As a result of the variation principle, KS/INV values are higher than KS/KS energies for which the self-consistency was allowed. The error caused by the HF approximation of the KS density in the KS equations approximately corresponds to the change caused by the use of the KS determinant in the HF energy expression. For example, for the ^3C atom, $E_{KS/MP0} - E_{HF/MP0} = 0.0041$ and $E_{KS/INV} - E_{KS/KS} = 0.0033$; for H_2O these values are 0.0069 and 0.0066 hartrees, respectively. Clearly, the KS/INV energies are very close to the solution of fully converged KS equations, which can be used for savings of computer time when HF densities are available: namely, the implementations of the hybrid DFT methods requires longer computational time then sole HF equations. Typically, in cases where a small error in energy is acceptable, elimination of the self-consistent procedure would reduce the computational time by 5–10 times. Also, construction of DFT functionals based on HF density (and hence independent of the actual DFT model) comes in mind as a possible application in the future. On the other hand, self-consistency is currently not the main limiting factor in computational quantum chemistry.[21]

TABLE I.
Molecular Energies (Negative).

	HF		KS/SVWN				KS/BPW91			
	MP0	MP2	KS	MP0	MP1	MP2	KS	MP0	MP1	MP2
^{3}C	37.6892	37.7649	37.5772	37.6851	37.6893	37.8096	37.8432	37.6851	37.6893	37.8096
^{3}O	74.8053	74.9426	74.6709	74.7950	74.8057	74.9966	75.0732	74.7999	74.8054	74.9941
^{4}N	54.3981	54.4970	54.2600	54.3905	54.3985	54.5369	54.5891	54.3940	54.3982	54.5360
N_2	108.9643	109.3420	108.9498	108.9389	108.9682	109.6244	109.5496	108.9463	108.9684	109.6197
CO	112.7669	113.1200	112.7303	112.7393	112.7750	113.3762	113.3354	112.7471	112.7742	113.3696
CO_2	187.6826	188.2683	187.6785	187.6288	187.7029	188.6972	188.6356	187.6420	187.7009	188.6841
F_2	198.7283	199.2108	198.6647	198.6954	198.7313	199.4859	199.5567	198.7054	198.7312	199.4777
H_2O	76.0463	76.2886	76.0812	76.0338	76.0475	76.4069	76.4398	76.0378	76.0475	76.4044
HF	100.0467	100.2943	100.0191	100.0341	100.0478	100.3994	100.4608	100.0385	100.0477	100.3969
a	−0.327	−0.049	−0.360	−0.348	−0.322	0.128	0.134	−0.342	−0.323	0.123

	KS/B3LYP				HF		
	KS	MP0	MP1	MP2	INV	QCISD/T	QCISD/T^a
^{3}C	37.8566	37.6851	37.6893	37.8096	37.8533	37.7684	37.7827
^{3}O	75.0862	74.8006	74.8053	74.9815	75.0816	74.9383	74.9815
^{4}N	54.5993	54.3945	54.3981	54.5260	54.5957	54.4942	54.5182
N_2	109.5557	108.9504	108.9665	109.5348	109.5425	109.3015	109.3841
CO	113.3474	112.7522	112.7700	113.2925	113.3334	113.0999	113.1667
CO_2	188.6428	187.6533	187.6897	188.5553	188.6155	188.2003	188.3486
F_2	199.5652	198.7114	198.7296	199.3992	199.5490	199.1734	199.3225
H_2O	76.4482	76.0394	76.0470	76.3740	76.4416	76.2749	76.3446
HF	100.4707	100.0402	100.0472	100.3706	100.4645	100.2757	100.3536
a	0.141	−0.338	−0.325	0.072	0.131	−0.073	0

The perturbation models are KS, eq. (4); MP0, eq. (8); MP1, eqs. (8) and (9); MP2, eqs. (8)–(10); and INV, eq. (11). The 6-311G** basis set was used with HF/MP2/6-311G** geometries; the symbol *a* denotes an average deviation with respect to the last (QCISD/T/aug-cc-pVTZ) calculation ($a = 1 - \sum_i x_i y_i / \sum x_i^2$) in %.

^{a} In the aug-cc-pVTZ basis.

ENERGY DISTRIBUTION

One of the biggest advantages of KS equations is a more balanced treatment of individual energy components.[15] In contrast, HF formalism leads to unbalanced distribution of the kinetic and potential energies. Individual energy parts for our systems can be conveniently analyzed using the MP0 expression in eq. (8). The differences in total, kinetic, and potential energies for both the KS and HF determinants are given in Table II. Note however that eq. (8) does not provide the correlation energy. Supposing that the KS/MP0 kinetic energies are more accurate, an underestimation of this component by HF theory can be observed for all cases. This is partially compensated by uniformly weaker electron-nuclear attraction in the HF model, while no obvious correlation can be found between KS and HF electron–electron interaction energy. Individual energy components are not experimentally observable and calculated differences in HF and KS kinetic energies are smaller than 1% of the total energy. Nevertheless, these variations may be important for studies where the kinetic energy is treated separately,[28] because the differences are comparable to energy changes in most chemical processes. It is remarkable that such an imbalance results in rather small changes in total energies. For example, KS and HF MP0 energies of CO_2 differ by 18 kcal/mol, while the difference of the nuclear–electron attraction is 35 times bigger.

TABLE II.
Total (E), Kinetic (T), Electron–Nuclear (V_{eN}), and Electron–Electron Coulombic (V_{ee}/C) and Exchange (V_{ee}/X) Energy Differences between MP0 [eq. (8)] Values Obtained with KS and HF Determinants (kcal/mol).

	ΔE	ΔT	ΔV_{eN}	$\Delta V_{ee}/C$	$\Delta V_{ee}/X$
^{3}C	3	17	−43	14	15
^{3}O	3	40	−59	−1	23
^{4}N	2	24	−40	−1	20
N_2	9	230	−464	246	−4
CO	9	180	−308	96	42
CO_2	18	328	−638	313	15
F_2	11	266	−400	−45	−5
H_2O	4	129	−174	45	5
HF	4	115	−130	4	15

ATOMIZATION ENERGIES

Atomization energies for six small molecules are listed in Table III and are organized analogously to Table I. The energies are related to experimental values from ref. 29. Similar to the absolute energies, the KS/MP0 and KS/MP1 values are qualitatively similar to the HF limit. However, the KS/MP2 perturbation correction leads to an overestimation of the atomization energies by about 40–50%. These results are in accord with observations in ref. 16 in which more sophisticated perturbation approaches are also proposed for DFT. Similar systematic error is absent for the HF/MP2 computation, which may be performed with approximately the same computer cost. Nevertheless, the computation of the KS/MP2 correction is still beneficial if compared to the MP0 and MP1 values.

The inverse process leads to an acceptable error of a few percent in KS energies (cf. 200 instead of 224 kcal/mol for N_2, etc.), which could be explored in practical calculations as discussed in the Theory Section. Similar to the atomization energies, one can observe the approximate relation

$$E_{KS/MP0} - E_{HF/MP0} \sim E_{KS/INV} - E_{KS/KS},$$

which may be explained as a result of the similarity between the HF and KS Hamiltonian and the linear dependence of energy on a small variation of density [see eqs. (4), (8), and (11)].

VIBRATIONAL ENERGIES

A more complex behavior of the KS determinant can be observed for calculation of the vibra-

tional frequencies. Their values for CO, HF, and N_2 molecules were calculated using a seven-point fit of the potential energy surface and are given in Table IV for the BPW91/6-311G** approximation. Other functionals and bases did not lead to qualitatively different results. For the frequencies the KS/MP1 correction provided a significant improvement: the shift of about 60–150 cm^{-1} in the three examples would be important for a comparison with the experiment.

In spite of the improvement of the absolute energies in the vicinity of the equilibrium distance, quite a defective potential surface was obtained with the KS/MP2 calculation. This is demonstrated in Figure 1 for the N_2 molecule. A reasonable shape of the potential well in the vicinity of the equilibrium distance was obtained with the HF/MP2 approximation, except for the divergence from the expected curve at distances greater than about 2 Å. On the contrary, the DFT/MP2 gradient was negative for all distances and no energy minimum exists for this model. The divergence, which is a sharp drop of the energy also observed for the HF/MP2 computation, starts already at the distance of about 1.6 Å. Clearly, the KS/MP2 perturbation correction is not suitable for calculation of potential energy surface.

EXCITATION ENERGIES

As mentioned in the Introduction, the one-determinant approximation can be encountered most frequently in the modeling of excited electronic states. In particular, frozen ground state KS or HF orbitals with different electron configurations are often adopted to evaluate molecular energies. Because such states are mutually orthogonal, this approach can be viewed as a zero-point approximation corresponding to the MP0 energy in eq. (8). The determinant therein is replaced by an appropriate spin-adapted wave function. Because of the numerical instability observed for the ground state, a little benefit of the higher MP1 and MP2 perturbation corrections may be expected. However, the knowledge of the properties of the diagonal MP0 terms may be important for further variational treatment of the wave functions.

In this section the excitation energies are estimated for formaldehyde, acetone, and CH_2 molecules. Equilibrium MP2/6-311G** geometries and a relatively large cc-pVTZ basis set involving a set of f orbitals were used. Table V lists the computed energies of the lowest four singlet and five triplet transitions in formaldehyde and compares them to experimental values. Apparently the KS deter-

TABLE III.
Atomization Energies (kcal/mol).

| KS/SVWN | HF | | KS/BPW91 | | | | KS/SVWN | | | |
	MP0	MP2	KS	MP0	MP1	MP2	KS	MP0	MP1	MP2
N_2	105	218	233	99	108	343	270	99	107	345
CO	171	259	263	164	175	355	303	165	176	357
CO_2	240	388	405	224	251	556	479	226	252	560
F_2	−41	30	47	−45	−40	117	75	−45	−40	119
H_2O	152	217	225	150	152	258	262	151	152	258
HF	94	133	136	93	95	156	157	45	94	158
a	−38	0	4	−41	−36	40	22	−43	−36	41

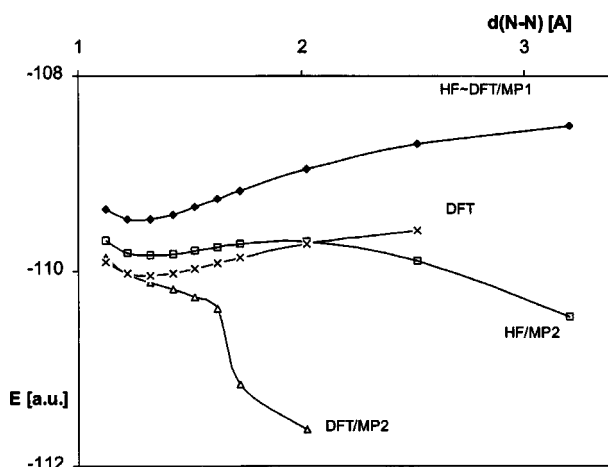| | KS/B3LYP | | | | HF | |
	KS	MP0	MP1	MP2	INV	Expt[29]
N_2	224	101	107	303	220	225
CO	254	167	173	323	250	256
CO_2	385	230	245	500	376	382
F_2	35	−45	−40	86	31	37
H_2O	224	151	152	247	224	219
HF	134	94	94	151	134	135
a	0	−40	−37	27	−1	0

The energies are without zero-point energy (deviation *a* defined as in Table I) with respect to the experimental values.

TABLE IV.
Vibrational Frequencies (cm^{-1}).

| | HF | | BPW91 | | | | |
	MP0	MP2	KS	MP0	MP1	MP2	Expt[28]
CO	2431	2086	2085	2506	2345	—	2143
HF	4363	4087	3840	4428	4333	3146	3962
N_2	2771	2117	2307	2810	2749	—	2331

FIGURE 1. Potential energy surface of the N_2 molecule as calculated by the HF and KS methods and by the three perturbation calculations.

minants of the three DFT approximations behave similarly and readily differ from the HF determinant. The KS energies of both the singlet and triplet transitions between the border orbitals (HOMO → LUMO, 8 → 9) are particularly significantly closer to the experiment. Higher frequency excitations are reproduced with similar errors by the KS and HF methods. The triplet 7 → 9 transition is (probably by an accident) best given by the HF computation.

The superiority of the KS determinant for modeling of excited states is also apparent for acetone and CH_2 molecules as can be seen in Table VI. The ener-

gies of the singlet HOMO → LUMO transitions for acetone and CH_2 are by 102 and 253 nm closer to the experiment (to a full CI calculation for CH_2), respectively, than if calculated with the HF determinant. Similar to formaldehyde, the difference between the

TABLE V.
Excitation Energies in Formaldehyde (nm).

Transition		HF	KS$_{LDA}$	KS$_{B3L}$	KS$_{BPW}$	Expt[30]
$^1A_2$	$8 \to 9$	232	265	265	266	302
$^1B_2$	$8 \to 10$	121	118	120	117	174
$^1A_1$	$8 \to 11$	101	99	101	99	152
$^1B_2$	$8 \to 12$	106	108	108	108	155
$^3A_2$	$8 \to 9$	265	316	314	317	354
$^3A_1$	$7 \to 9$	206	257	249	256	207
$^3B_2$	$8 \to 10$	126	125	126	124	175
$^3A_1$	$8 \to 11$	108	110	110	110	152
$^3B_2$	$8 \to 12$	109	113	113	113	157

cc-pVTZ basis, MP2/6-311G** geometry.

KS and HF energies becomes insignificant for higher energy transitions. Only for the $16 \to 18$ excitation in acetone was a significantly more accurate value obtained by the HF method. However, in a smaller 6-311++G** basis, a better energy was obtained with the KS approximation for this case. Such a numerical instability indicates that a full variational rather than the rigid-determinant treatment should be used for this transition. The sharp deterioration of the HF excitation energies for the bigger system (acetone), as well as the relative stability of the error of the KS approximation, is in accord with results observed for other molecules.[8]

Conclusions

KS and HF determinants provided similar values of molecular properties when used as the true many-body wave functions in first-order perturbation formulas (MP0). Greater differences were observed for the second-order perturbations (MP1, MP2). The KS/MP1 correction is small and can be omitted for most applications. The MP2 correction applied to the KS determinant is less accurate than the usual HF/MP2 method. This indicates a slower convergence of the perturbation expansions based on the KS determinant. On the other hand, the KS determinant (rigid orbitals formally used in the first-order perturbation approach) is more suitable for approximations of the lowest energy excited electronic states. The results are in accord with previous observations where sum over states modeling of electronic states with the KS wave function provided better values of molecular property tensors than the HF approximation.

TABLE VI.
Excitation Energies for Acetone and CH$_2$ (nm).

Transition		HF	KS$_{B3L}$	Expt[30]
Acetone				
$^1A_2$	$16 \to 17$	126	228	280
$^1B_2$	$16 \to 18$	176	125	195
$^1A_1$	$16 \to 19$	107	105	167
$^1A_2$	$14 \to 17$	97	109	168
$^1B_2$	$16 \to 20$	105	105	166
$^1A_2$	$16 \to 21$	115	106	153
$^3A_2$	$16 \to 17$	127	258	297
$^3A_1$	$15 \to 17$	105	189	211
$^3A_2$	$14 \to 17$	98	111	198
$^3A_2$	$16 \to 21$	117	107	157
CH$_2$				FCI[31]
$^1B_2$	$4 \to 5$	633	886	691
$^1A_1$	$4 \to 6$	148	155	266
$^1A_2$	$3 \to 5$	167	183	212
$^1A_1$	$4 \to 9$	82	84	190
$^1B_1$	$4 \to 7$	123	128	161
$^1B_1$	$3 \to 6$	91	93	155
$^1A_1$	$3 \to 7$	76	77	146
$^1B_2$	$4 \to 10$	85	85	139
$^1A_2$	$3 \to 10$	61	61	131
$^1B_2$	$2 \to 5$	72	72	117

cc-pVTZ basis, MP2/6-311G** geometry.

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