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Parity-violating interaction in H₂O₂ calculated from density-functional theory

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Abstract

The calculation of parity-violating interactions has been implemented within the framework of nonrelativistic density-functional theory. Different exchange–correlation functionals have been tested for H₂O₂ and are compared with Hartree–Fock and complete-active-space multiconfigurational self-consistent field calculations. At all levels of theory, *p*-type Gaussian basis functions are found to be important. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the discovery of parity-violating (PV) processes in the 1950s [1], it has been suggested that the PV interaction could play a role in the selection of the particular chirality found in nature for molecules such as sugars and aminoacids. Later, in the 1980s, it was found that the energy differences between the chiral forms of these molecules appear to be extremely small (of the order of 10⁻²⁰ E_h) [2], although it was proposed that the PV energy difference between enantiomers can be measured spectroscopically [3] and also that PV effects in nuclear-magnetic resonance (NMR) spectra might be measurable [4]. More recently, there has been a considerable, renewed interest in

the possibly accurate ab initio computation of PV interactions of chiral molecules. Much work in this field has been conducted by Quack, Lazzeretti, and Schwerdtfeger and their coworkers [5–16], in particular at the nonrelativistic and relativistic (Dirac-)Hartree–Fock and multiconfigurational self-consistent field (MCSCF) levels. By contrast, density-functional theory (DFT) has not yet been considered for the calculation of PV interactions, even though such calculations might help to investigate larger molecules with heavier nuclei, for which the PV interactions could be larger than in the relatively small molecules that have so far been studied by the nonrelativistic Hartree–Fock and MCSCF methods and by relativistic four-component methods.

In the present Letter, we report the implementation of the computation of PV interactions at the Kohn–Sham level of theory. To compare with previous work, we have chosen as our model system H₂O₂.

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2. Theory and method

2.1. PV linear-response theory

Within a nonrelativistic framework, the PV interaction between the n electrons and N nuclei of a molecular system is represented by the operator (see [9] and references therein):

$$\begin{aligned} H_{\text{pv}} = & \frac{G_F \alpha}{2\sqrt{2}} \sum_{A=1}^N [Z_A(1 - 4\sin^2 \theta_w) - N_A] \\ & \times \sum_{i=1}^n [\mathbf{p}_i \cdot \mathbf{s}_i, \delta(\mathbf{r}_{iA})]_+ - \frac{G_F \alpha}{2\sqrt{2}} \sum_{A=1}^N \lambda_A(1 - 4\sin^2 \theta_w) \\ & \times \sum_{i=1}^n ([\mathbf{p}_i \cdot \mathbf{I}_A, \delta(\mathbf{r}_{iA})]_+ + 2i[\mathbf{p}_i, \delta(\mathbf{r}_{iA})] \cdot \mathbf{I}_A \times \mathbf{s}_i). \end{aligned} \quad (1)$$

Here $G_F \approx 2.22254 \times 10^{-14}$ a.u. is the Fermi constant, $\alpha \approx 7.2974 \times 10^{-3}$ is the fine-structure constant, Z_A the number of protons, N_A the number of neutrons, λ_A a numerical constant close to one, \mathbf{I}_A the nuclear spin, and $\sin^2 \theta_w$ the Weinberg parameter. It is common practice to use the theoretical value of the Weinberg parameter of $\sin^2 \theta_w = 0.25$ in Eq. (1) (omitting summation ranges):

$$H_{\text{pv}}^{\text{eff}} = -\frac{G_F \alpha}{2\sqrt{2}} \sum_A N_A \sum_i [\mathbf{p}_i \cdot \mathbf{s}_i, \delta(\mathbf{r}_{iA})]_+. \quad (2)$$

This is the effective PV operator implemented in our program.

Since the expectation value of H_{pv} for a non-relativistic wave function vanishes, we need to include a complex relativistic operator that couples the singlet ground state to the triplet excited states. For a perturbational treatment (as in linear-response theory), the first-order spin-orbit operator is the obvious choice. In atomic units, the full spin-orbit interaction operator is given by

$$\begin{aligned} H_{\text{SO}} = & \frac{\alpha^2}{2} \sum_A Z_A \sum_i \frac{\mathbf{l}_{iA} \cdot \mathbf{s}_i}{r_{iA}^3} \\ & + \frac{\alpha^2}{2} \sum_{i,j} \frac{\mathbf{l}_{ij} \cdot (\mathbf{s}_i + 2\mathbf{s}_j)}{r_{ij}^3}, \end{aligned} \quad (3)$$

where $\mathbf{l}_{i,A}$ is the angular momentum of electron i relative to the position of nucleus A ; likewise, $\mathbf{l}_{i,j}$ is

the angular momentum of electron i relative to electron j . The two-electron spin-orbit operator is avoided by introducing an effective one-electron spin-orbit operator

$$H_{\text{SO}}^{\text{eff}} = \frac{\alpha^2}{2} \sum_A \eta_A Z_A \sum_i \frac{\mathbf{l}_{iA} \cdot \mathbf{s}_i}{r_{iA}^3}, \quad (4)$$

where η_A is some empirical parameter [9], see also [17,18]. In our DFT implementation, we shall use this effective operator, thereby avoiding the difficulties associated with the treatment of two-electron operators in Kohn–Sham theory. Following [9], we use $\eta_A = 0.66$ for all atoms.

Using standard linear-response theory, the PV interaction may now be calculated from the effective operators Eqs. (2) and (4) according to the expression

$$E_{\text{pv}} = \langle\langle H_{\text{pv}}^{\text{eff}}, H_{\text{SO}}^{\text{eff}} \rangle\rangle. \quad (5)$$

Our implementation of DFT linear-response theory follows the general framework of the DALTON package [19], noting that the PV interaction involves triplet perturbations. In our development version of Dalton, DFT singlet and triplet linear-response theory has already been implemented for the calculation of NMR nuclear shielding and indirect spin–spin coupling constants – see [20,21]. In the present version of Dalton, three functionals are available: the local density approximation (LDA) functional [22,23], the gradient-corrected Becke–Lee–Yang–Parr (BLYP) functional [24,25], and the hybrid functional B3LYP (three-parameter hybrid BLYP) [26,27]. The DFT implementation in Dalton is based on that in CADPAC [28], using the same routines for the generation of abscissas and weights of the numerical quadrature and for the evaluation of the functionals.

2.2. PV integral evaluation

The spin-orbit integrals of $H_{\text{SO}}^{\text{eff}}$ in Eq. (4) are present in the DALTON program, see [29]. The integrals of $H_{\text{PV}}^{\text{eff}}$ in Eq. (2) are not part of the official Dalton release, although they have previously been implemented by Berger and Quack in their local version of Dalton [9]. These integrals

have been reimplemented by us for later release in Dalton, in a manner that allows the use of finite nuclei. Since our implementation also includes a useful technique for the calculation of Dirac delta-function integrals within the McMurchie–Davidson scheme [30], it is described here.

For the integration over the PV operator Eq. (2), we need to evaluate the spatial integrals $\langle a|[\delta(\mathbf{r}_C), \nabla]_+|b\rangle$ over Gaussian orbitals. Introducing the gradient operators ∇_A and ∇_B with respect to the positions \mathbf{A} and \mathbf{B} of the Gaussians a and b , respectively, and likewise the operator ∇_P with respect to the center of the overlap distribution

$$\mathbf{P} = \frac{\zeta_a \mathbf{A} + \zeta_b \mathbf{B}}{\zeta_a + \zeta_b}, \quad (6)$$

where ζ_a and ζ_b are the Gaussian exponents, we find that $\langle a|[\delta(\mathbf{r}_C), \nabla]_+|b\rangle$ may be written in the following equivalent ways:

$$\langle a|[\delta(\mathbf{r}_C), \nabla]_+|b\rangle = (\nabla_A - \nabla_B)\langle a|\delta(\mathbf{r}_C)|b\rangle \quad (7)$$

$$= (2\nabla_A - \nabla_P)\langle a|\delta(\mathbf{r}_C)|b\rangle \quad (8)$$

$$= -\frac{\nabla_P^2}{4\pi}(2\nabla_A - \nabla_P)\left\langle a\left|\frac{1}{r_C}\right|b\right\rangle. \quad (9)$$

In going from Eq. (8) to Eq. (9), we have made use of the relation $\nabla^2(1/r_C) = -4\pi\delta(\mathbf{r}_C)$.

In our implementation, we have used the form Eq. (8). We compute the Dirac delta-function integrals over Gaussian orbitals by expanding the overlap charge distribution of the two Gaussians in a basis of Hermite functions,

$$\langle a|\delta(\mathbf{r}_C)|b\rangle = \sum_{tuv} E_{tuv} \Delta_{tuv}, \quad (10)$$

where E_{tuv} are the usual expansion coefficients and Δ_{tuv} the Dirac delta-function integrals over Hermite functions [31]. The latter are computed from the recurrence relations

$$\Delta_{000} = \exp(-\zeta_p R_{CP}^2), \quad (11)$$

$$\Delta_{t+1,uv} = 2\zeta_p(X_{CP}\Delta_{tuv} - t\Delta_{t-1,uv}), \quad (12)$$

$$\Delta_{t,u+1,v} = 2\zeta_p(Y_{CP}\Delta_{tuv} - u\Delta_{t,u-1,v}), \quad (13)$$

$$\Delta_{tu,v+1} = 2\zeta_p(Z_{CP}\Delta_{tuv} - v\Delta_{tu,v-1}). \quad (14)$$

Here $\zeta_p = \zeta_a + \zeta_b$, and X_{CP} , Y_{CP} , and Z_{CP} are the Cartesian components of $\mathbf{R}_{CP} = \mathbf{C} - \mathbf{P}$.

The above integrals refer to point-shaped nuclei. It is straightforward to extend the calculation of PV interactions to nuclei that are described by normalized Gaussian distributions of the form

$$G_\eta(r_C) = \left(\frac{\eta}{\pi}\right)^{3/2} \exp(-\eta r_C^2). \quad (15)$$

In this case, the following one-electron integrals occur:

$$\langle a|[G_\eta(r_C), \nabla]_+|b\rangle = (\nabla_A - \nabla_B)\langle a|G_\eta(r_C)|b\rangle \quad (16)$$

$$= (2\nabla_A - \nabla_P)\langle a|G_\eta(r_C)|b\rangle \quad (17)$$

$$= -\frac{\nabla_P^2}{4\pi}(2\nabla_A - \nabla_P)\left\langle a\left|\frac{\text{erf}(\sqrt{\eta}r_C)}{r_C}\right|b\right\rangle. \quad (18)$$

We use Eq. (18) when we need the integrals for Gaussian-shaped nuclei, simply because the necessary integrals over the operator $\text{erf}(\sqrt{\eta}r_C)/r_C$ are available in the DALTON program from an earlier implementation of the one-electron spatial finite-nucleus spin-orbit integrals, which are computed from the expression [32]

$$\nabla_P \times \nabla_B \left\langle a\left|\frac{\text{erf}(\sqrt{\eta}r_C)}{r_C}\right|b\right\rangle. \quad (19)$$

Only minor modifications of the computer implementation of the standard nuclear-attraction integrals are needed to obtain the integrals over the operator $\text{erf}(\sqrt{\eta}r_C)/r_C$. When the nuclear-attraction integrals are computed from the Boys functions $F_m(\zeta_p R_{CP}^2)$, where

$$F_m(W) = \int_0^1 t^{2m} e^{-Wt^2} dt, \quad (20)$$

then the new integrals over $\text{erf}(\sqrt{\eta}r_C)/r_C$ are obtained by scaling the arguments of the Boys functions by $\eta/(\eta + \zeta_p)$ and the function values by $[\eta/(\eta + \zeta_p)]^{1/2}$. Hence,

$$F_m(\zeta_p R_{CP}^2) \rightarrow \left\langle a\left|\frac{1}{r_C}\right|b\right\rangle, \quad (21)$$

$$\sqrt{\frac{\eta}{\eta + \zeta_p}} F_m\left(\frac{\eta \zeta_p}{\eta + \zeta_p} R_{CP}^2\right) \rightarrow \left\langle a\left|\frac{\text{erf}(\sqrt{\eta}r_C)}{r_C}\right|b\right\rangle. \quad (22)$$

3. Calculations

3.1. Computational details

All calculations have been performed with a local development version of the DALTON program [19], using spherical components of the Gaussian basis functions. The bond lengths and bond angles of H_2O_2 have been kept fixed at the values $R_{\text{O}-\text{O}} = 149.0$ pm, $R_{\text{O}-\text{H}} = 97.0$ pm, and $\angle_{\text{O}-\text{O}-\text{H}} = 100.0^\circ$. Unless otherwise noted, the B3LYP functional is used for the calculations in the present work. The PV interactions are calculated for the isotopes ^1H and ^{16}O .

3.2. Basis-set convergence

In Table 1, we have, for a variety of basis sets, listed the B3LYP and Hartree–Fock ground-state energies and PV interactions in H_2O_2 at a torsional angle of 45° . In addition, we have in Fig. 1 plotted the PV interaction as a function of the cardinal

number X for the basis sets cc-pV X Z, aug-cc-pV X Z, and cc-pCV X Z at the B3LYP and Hartree–Fock levels of theory.

At both levels of theory, the PV interaction is severely underestimated by the smallest basis sets. Moreover, the magnitude of the interaction increases uniformly with the cardinal number. Thus, whereas the PV/B3LYP interaction is only $-31.4 \times 10^{-20} E_{\text{h}}$ in the cc-pVDZ basis, it is as large as $-51.9 \times 10^{-20} E_{\text{h}}$ in the cc-pV6Z basis. Nevertheless, convergence has not been reached, even in the very large cc-pV6Z basis – see Fig. 1. Clearly, the functions that are added to the cc-pV X Z basis sets as we increase the cardinal number are not those that are needed for an accurate description of the PV interaction. We also note that the aug-cc-pV X Z and cc-pCV X Z basis sets (augmented with diffuse and steep functions, respectively) do not perform much better than the parent basis sets cc-pV X Z, at least for high cardinal numbers.

The convergence of the standard basis sets for the calculation of the PV interaction is improved

Table 1
Total energy (E) and PV interaction (E_{pv}) of H_2O_2 with a torsional angle of 45°

Basis	B3LYP		Hartree–Fock	
	E/E_{h}	$E_{\text{pv}}/(10^{-20} E_{\text{h}})$	E/E_{h}	$E_{\text{pv}}/(10^{-20} E_{\text{h}})$
STO-3G	-149.364919	-10.175	-148.745175	-9.429
6-31G	-151.409129	-32.090	-150.693878	-39.059
Huz-II	-151.521679	-42.909	-150.807979	-49.780
Huz-III	-151.549576	-47.947	-150.831671	-54.936
Huz-IV	-151.553773	-45.885	-150.836471	-52.289
cc-pVDZ	-151.474813	-31.442	-150.772170	-37.439
cc-pVTZ	-151.536331	-39.926	-150.824130	-46.078
cc-pVQZ	-151.551375	-44.813	-150.836413	-51.737
cc-pV5Z	-151.556571	-49.304	-150.839747	-56.912
cc-pV6Z	-151.557486	-51.860	-150.840167	-59.596
cc-pCVDZ	-151.477766	-35.312	-150.772819	-41.752
cc-pCVTZ	-151.538702	-41.668	-150.824651	-47.164
cc-pCVQZ	-151.552773	-46.118	-150.836622	-52.424
cc-pCV5Z	-151.556960	-49.410	-150.839774	-56.323
aug-cc-pVDZ	-151.503361	-30.969	-150.789973	-37.074
aug-cc-pVTZ	-151.542770	-39.203	-150.827610	-45.569
aug-cc-pVQZ	-151.553846	-44.740	-150.837480	-51.714
aug-cc-pV5Z	-151.557106	-49.507	-150.839967	-57.056
aug-cc-pCVDZ	-151.505958	-35.343	-150.790549	-41.721
aug-cc-pCVTZ	-151.545171	-41.326	-150.828082	-47.028
aug-cc-pCVQZ	-151.555090	-45.943	-150.837665	-52.380
aug-cc-pCV5Z	-151.557486	-49.430	-150.839993	-56.330
4-comp QZ [8]				-58.92

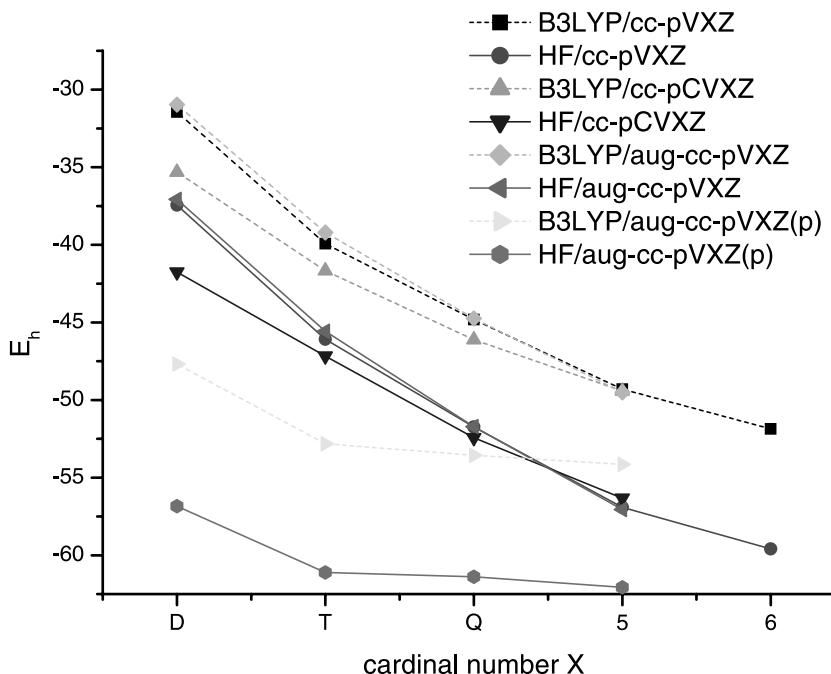


Fig. 1. Basis-set convergence of the PV interaction.

by adding steep p functions, as demonstrated by Laerdahl et al. [8] in their relativistic four-component approach. Such functions may be added in a variety of ways – see Table 2. One possibility is to uncontract the original p set and to add new sets of p functions in an even-tempered manner, in the same way as improved s basis sets are generated in the calculation of indirect nuclear spin–spin coupling constants. A different approach is simply to include in the p basis all functions from the s basis with an exponent higher than the highest exponent in the original p basis. Based on the reasonable but somewhat arbitrary assumption that the best basis set gives the strongest interaction, this approach gives better results than does the even-tempered extension. In Fig. 1, we have also plotted the PV interaction obtained with such aug-cc-pVXZ+p(s) basis sets. The convergence rate is now much more satisfactory, with convergence reached already at the triple-zeta level.

The importance of adding steep p functions can be understood from a consideration of the PV interaction operator Eq. (2), whose spatial part is

given by Eq. (7). Disregarding the (small) many-center contributions, these integrals are nonzero only when the total angular momentum is equal to one – that is, when one of the Gaussians a and b is an s function and the other a p function. Moreover, the largest integrals arise from steep (i.e., compact) s and p functions. Finally, a balanced treatment of the s and p spaces with respect to the calculation of PV interactions is ensured when the (steep) s and p functions have the same exponents.

Further basis-set investigations (see Table 2) confirm that little or nothing is gained by adding steep d functions or additional steep s functions to the basis. Moreover, since most of the PV interaction arises from the oxygen nuclei, little is achieved by adding steep p functions to the hydrogen atoms. The efficacy of including the steep s functions in the p space is demonstrated by the calculations with the small 6-31G+p(s) basis, which produces PV interactions similar to those obtained with much larger basis sets.

Table 2

Ground-state energy (E) and PV interaction (E_{pv}) of H_2O_2 with a fixed torsional angle of 45° , obtained using basis sets augmented with steep p functions

Basis	B3LYP		Hartree–Fock	
	E/E_h	$E_{\text{pv}}/(10^{-20} E_h)$	E/E_h	$E_{\text{pv}}/(10^{-20} E_h)$
6-31G+p(s)	-151.440861	-54.074	-150.723842	-65.569
Huz-II+p(s)	-151.525784	-57.176	-150.811864	-65.906
Huz-III+p(s)	-151.550156	-57.283	-150.832232	-65.593
Huz-IV+p(s)	-151.554369	-54.545	-150.837002	-62.104
u-Huz-IV	-151.553777	-45.836	-150.836503	-52.245
u-Huz-IV+3s(6) (oxygen only)	-151.554116	-46.389	-150.836811	-52.884
u-Huz-IV+3p(6) (oxygen only)	-151.554246	-54.178	-150.836891	-61.744
u-Huz-IV+3p(s) (oxygen only)	-151.554062	-54.825	-150.836731	-62.478
u-Huz-IV+3p(s)	-151.554062	-54.837	-150.836872	-62.469
u-Huz-IV+1d ^a (oxygen only)	-151.553801	-45.830	-150.836502	-52.245
aug-cc-pVDZ+p(s)	-151.519494	-47.676	-150.804365	-56.842
aug-cc-pVTZ+p(s)	-151.546155	-52.816	-150.830584	-61.106
aug-cc-pVQZ+p(s)	-151.554591	-53.563	-150.838155	-61.383
aug-cc-pV5Z+np(s)	-151.557164	-54.149	-150.840021	-62.065

The basis sets labeled u- are uncontracted sets and in the basis sets labeled +p(s), we have included in the p basis all s functions whose exponent is higher than the highest exponent of the original p basis. The +ms(x) and +mp(x) labels show that we have added m steep s and p functions, respectively, in an even-tempered manner, by multiplying the highest exponents by the factor x .

^a d -exponent 28.96.

3.3. PV dependence on torsional angle

In Table 3, we have listed the PV interaction as a function of the dihedral angle for different computational models and basis sets. In Fig. 2, the B3LYP functional is compared with the Hartree–Fock and complete-active-space MCSCF models (CASSCF), using the Huz-IV+p(s) basis set, generated from the Huz-IV basis set of Huzinaga [33]. In the CASSCF calculations, rather large active spaces have been obtained by distributing 14 electrons among 13 active orbitals.

The B3LYP curve follows closely the Hartree–Fock curve and also resembles the coupled-cluster curve in Fig. 1 of [14], calculated at the coupled-cluster singles-and-doubles (CCSD) level with a perturbative correction for triples (CCSD(T)). At the CCSD(T) level, the correlation contribution is about $10 \times 10^{-20} E_h$ at 45° ; at the B3LYP/aug-cc-pV5Z+np(s) level, the corresponding contribution is $8 \times 10^{-20} E_h$.

The CASSCF results are different from those obtained at the Hartree–Fock, B3LYP, and

CCSD(T) levels, with a smaller difference between the results at 45° and 135° . It is not clear whether this behavior of the CASSCF model is indicative of an inadequacy of the MCSCF model (inadequate treatment of dynamical correlation) or an inadequacy of the other models (inadequate treatment of static correlation). Nevertheless, from the comparison with CCSD(T), we tentatively conclude that the B3LYP model gives an adequate treatment of the effect of dynamical correlation on the PV interaction, but note that this point may require further investigation.

In Fig. 3, we compare the PV curves for different DFT functionals. The differences between the local functional, the gradient-corrected functional, and the hybrid functional are surprisingly small, for all dihedral angles.

3.4. Finite nuclei

In Table 4, we have listed PV interactions for finite Gaussian-shaped nuclei. To simplify matters, we have used the same Gaussian exponents for the

Table 3

PV interactions in H_2O_2 for different torsional angles ($10^{-20} E_h$)

Method	Basis	30°	60°	90°	120°	150°
Hartree-Fock	6-31G+p(s)	-59.9	-52.6	8.3	63.4	60.9
	Huz-II+p(s)	-59.2	-54.0	7.1	64.9	63.4
	Huz-III+p(s)	-58.9	-53.8	7.1	65.1	63.9
	Huz-IV+p(s)	-55.7	-50.9	6.8	61.8	60.5
	aug-cc-pVDZ+p(s)	-51.1	-46.5	6.9	57.7	56.3
	aug-cc-pVTZ+p(s)	-54.8	-50.2	6.8	61.0	59.5
	aug-cc-pVQZ+p(s)	-61.4	-50.4	6.7	61.0	59.7
B3LYP	6-31G+p(s)	-51.5	-39.1	22.1	74.4	67.1
	Huz-II+p(s)	-52.8	-43.9	17.6	73.6	68.7
	Huz-III+p(s)	-52.6	-44.5	15.8	71.4	67.5
	Huz-IV+p(s)	-50.0	-42.4	15.0	68.0	64.1
	aug-cc-pVDZ+p(s)	-43.8	-36.8	14.0	60.9	57.2
	aug-cc-pVTZ+p(s)	-48.4	-41.1	14.6	66.0	62.0
	aug-cc-pVQZ+p(s)	-49.1	-41.6	14.7	66.6	62.8
BLYP	Huz-II+p(s)	-50.1	-39.7	21.9	77.1	70.8
	Huz-III+p(s)	-50.2	-40.9	19.0	73.8	68.8
	Huz-IV+p(s)	-47.9	-39.2	18.0	70.3	65.4
LDA	Huz-II+p(s)	-53.8	-44.1	19.4	77.3	72.0
	Huz-III+p(s)	-52.8	-44.1	17.3	74.1	74.1
	Huz-IV+p(s)	-49.9	-41.7	16.5	70.3	65.4
CASSCF	Huz-III+p(s)	-48.2	-40.4	15.5	60.4	58.1
	Huz-IV+p(s)	-45.6	-38.2	14.8	64.8	54.8

In the CASSCF calculations, we have correlated 14 electrons in 13 orbitals, with the oxygen 1s orbitals frozen.

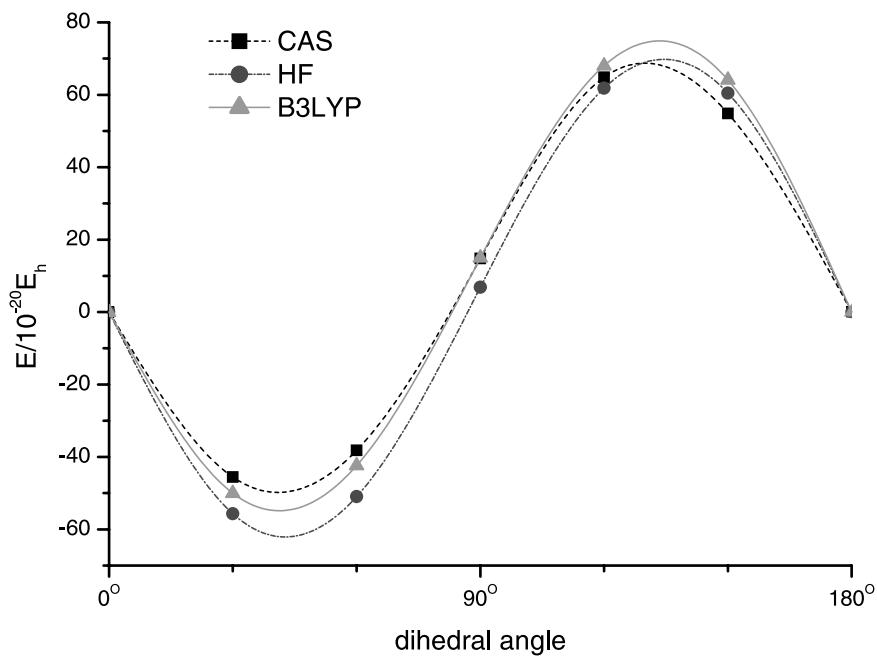


Fig. 2. PV interaction from the B3LYP functional compared with the Hartree-Fock and CASSCF results.

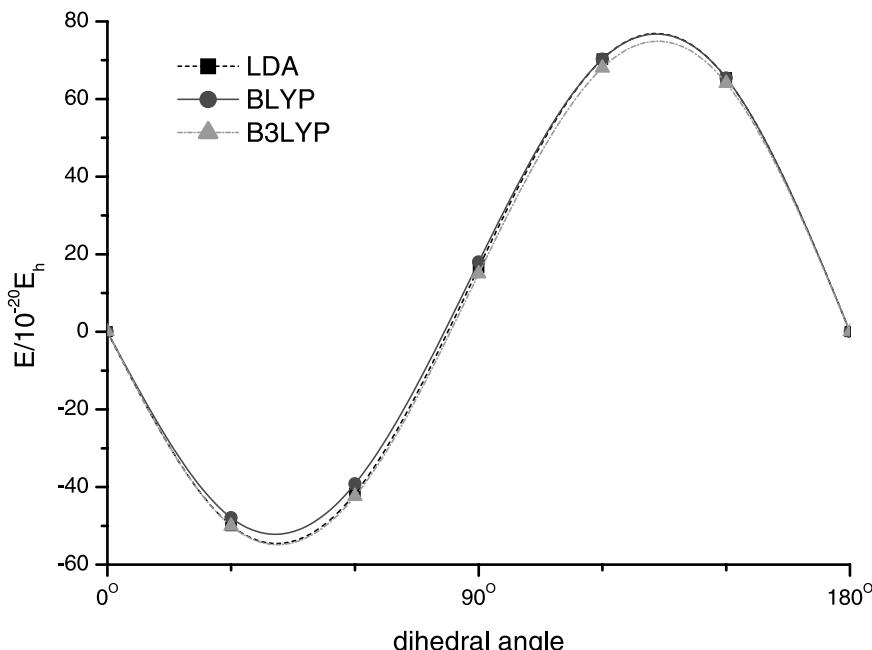


Fig. 3. PV interaction from the B3LYP, BLYP, and LDA functionals.

oxygen and hydrogen nuclei. The finite-nucleus effect reduces the magnitude of the PV interaction but becomes appreciable only for $\eta < 10^6 a_0^{-2}$. Since a realistic nuclear size of first-row atoms is

Table 4
PV interaction in H_2O_2 computed in the Huz-IV+p(s) basis as a function of the exponent η of the Gaussian nuclear model

$\log_{10}(\eta)$	$E_{pv}/(10^{-20} E_h)$	
	B3LYP	Hartree-Fock
∞	-54.544644	-62.104284
10.0	-54.544688	-62.104293
9.0	-54.544527	-62.104113
8.0	-54.542914	-62.102316
7.0	-54.526837	-62.084398
6.0	-54.371038	-61.910683
5.0	-53.174599	-60.571439
4.0	-48.890819	-55.722148
3.0	-37.130105	-42.403246
2.0	-15.300879	-17.591614
1.5	-5.7225121	-6.6221258
1.0	-1.1140021	-1.2984543
0.5	-0.0778206	-0.0926541

η has been chosen to be the same for O and H. The dihedral angle has been fixed at $\theta = 45^\circ$ and the Weinberg parameter has been chosen as $\sin^2 \theta_w = 0.25$.

$\eta \approx 10^9 a_0^{-2}$ [34], we conclude that the point-charge nuclear model is adequate for first-row atoms.

4. Conclusions

We have presented an implementation of linear-response theory for the calculation of PV interactions at the Kohn-Sham level of theory. Pilot calculations on H_2O_2 indicate that DFT provides an adequate model for the calculation of PV interactions, at least for molecules containing first-row atoms without large static-correlation effects. Moreover, the Kohn-Sham calculations appear not to be very sensitive to the choice of exchange-correlation functionals. In view of the low cost of the Kohn-Sham calculations, these results are promising for the calculation of PV interactions of large organic molecules.

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