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Multiconfiguration linear response approach to the calculation of parity violating potentials in polyatomic molecules

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We present a multiconfiguration linear response approach to electroweak quantum chemistry including effects from the parity violating weak nuclear force. Compared to our previous configuration interaction singles-restricted Hartree–Fock (CIS-RHF) approach [A. Bakasov, T. K. Ha, and M. Quack, J. Chem. Phys. **109**, 7263 (1998)], the parity violating potential E_{pv} is introduced by the linear response function and by solving the linear response equations in a direct iterative manner. Calculations are carried out within the multiconfiguration linear response approximation (MCLR) and its special cases, the configuration interaction approach (CI) and the random phase approximation (RPA). The systematic approach presented here, provides a systematic check and improvement upon various approximations used in the calculation of E_{pv}. Extensive results are obtained for hydrogen peroxide at the CISDT (CI singles, doubles and triples) and CISDTQ (CI singles, doubles, triples, and quadruples) as well as at the complete active space self-consistent-field–linear response (CASSCF–LR) level. We compare to carlier results at the CIS-RHF level and confirm the order of magnitude increase in E_{pv} reported earlier as compared to the widely used single determinant excitation-restricted Hartree–Fock (SDE-RHF) method. The new approach overcomes previous limitations for calculating E_{pv} with biradicaloid structures such as twisted ethylene, for which numerical results are presented. This allows us to calculate E_{pv} for a similar unsaturated system such as allene derivatives, which may be of experimental interest.
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I. INTRODUCTION

The discovery of parity violation[1,2] and the formulation of electroweak theory[3–5] quickly led to qualitative estimates of the effect of parity violation in atoms and molecules[6–11] as well as to quantitative quantum chemical calculations[12–20] (for more extensive review see Refs. 21 and 22). The large majority of the earlier calculations was based on the single determinant excitation-restricted Hartree–Fock (SDE-RHF) approach by Hegstrom *et al.*[15] leading to the first understanding of the magnitude of parity violating potentials, E_{pv}, in polyatomic molecules. Exciting results recently obtained with the configuration interaction singles-restricted Hartree–Fock (CIS-RHF) approach suggest that E_{pv} is actually an order of magnitude larger than previously predicted. This increase of E_{pv} by an order of magnitude has led to a completely changed outlook on the effects of parity violation.[21,22] For example, a larger value of E_{pv} has profound consequences for experiments proposed to measure effects of E_{pv} in chiral molecules[17,23–28] as well as for the possible role of parity violation in the evolution of biochemical homochirality.[8,14–17,24,27,29,30] While the results of Refs. 21 and 22 have already been qualitatively confirmed[31,32] with independent calculations[33] (see also Ref. 34), there is clearly a need for a systematic approach to ‘‘electroweak quantum chemistry’’ as we have called it.[21,22,35]

An important aspect of systematic approaches to quantum chemical calculations in general is the proper inclusion of electron correlation. Multiconfiguration methods are known to give an adequate qualitative and in the full-CI limit exact description of correlation effects. It is thus the aim of this paper to introduce a multiconfiguration linear response (MCLR) method for the calculation of E_{pv}, which satisfies the need for such a systematic approach, allowing one to study various successive levels of accuracy in the calculation and thereby to judge the validity of results from various, successive approximations.

In short, our new approach confirms that the major part of the increase in E_{pv} is indeed recovered by the CIS-RHF method.[21,22] However, the MCLR approach allows us to overcome some serious limitations of the CIS-RHF method, already previously noted for molecules with potentially biradicaloid structures such as twisted ethylene. The MCLR approach also overcomes the problem of convergence in the sum-over-states expression for E_{pv}. We briefly outline the general theory and computational strategy and then present selected results on molecular examples which may serve as test cases and benchmarks for comparison.

II. THEORY

A. General background

For completeness, we briefly present here the general equations used in the theory of parity violation in molecules. Much of this goes back to atomic[12,13] and molecular[14,15] calculations two decades ago, and we refer to Ref. 22 for a very detailed and careful recent description.

Within the nonrelativistic framework the parity violating

[a)] Author to whom correspondence should be addressed; electronic mail: quack@ir.phys.chem.ethz.ch electron–nucleus interaction operator $\hat{H}_{\mathrm{pv}}^{\mathrm{e-nucl}}$ of a molecular system with N nuclei and n electrons is given in atomic units by[12,13,15,17,22,35,36]

$$\begin{aligned}\hat{H}_{\mathrm{pv}}^{\mathrm{e-nucl}}&=\sum_{i=1}^{n}\hat{h}_{\mathrm{pv}}^{\mathrm{e-nucl}}(i)\\&=\sum_{i=1}^{n}[\hat{h}_{\mathrm{pv}}^{(1)}(i)+\hat{h}_{\mathrm{pv}}^{(2)}(i)+\hat{h}_{\mathrm{pv}}^{(3)}(i)]\\&=\frac{G_F\alpha}{2\sqrt{2}}\sum_{i=1}^{n}\left[\sum_{A=1}^{N}Q_w(A)\{\hat{\vec{p}}_i\cdot\hat{\vec{s}}_i,\delta^3(\vec{r}_i-\vec{r}_A)\}_+\right.\\&\quad+\sum_{A=1}^{N}(-\lambda_A)(1-4\sin^2\theta_w)\{\hat{\vec{p}}_i\cdot\hat{\vec{I}}_A,\delta^3(\vec{r}_i-\vec{r}_A)\}_+\\&\quad+\sum_{A=1}^{N}2i\lambda_A(1-4\sin^2\theta_w)\\&\quad\left.\times(\hat{\vec{s}}_i\times\hat{\vec{I}}_A)\cdot[\hat{\vec{p}}_i,\delta^3(\vec{r}_i-\vec{r}_A)]\right]\end{aligned}\tag{1}$$

with $G_F=2.222\,54\times10^{-14}$ E_h representing the Fermi constant,[22] α the fine structure constant, $Q_w(A)=Z_A(1-4\sin^2\theta_w)-N_A$, Z_A the number of protons in nucleus A, N_A its number of neutrons and $\hat{\vec{I}}_A$ its nuclear spin operator, $\sin^2\theta_w$ the Weinberg parameter, $\hat{\vec{p}}_i$ the linear momentum operator of electron i and $\hat{\vec{s}}_i$ its spin operator, $\delta^3(\vec{x})$ the Dirac delta distribution, $\vec{r}_\mu$ the position vector of particle μ, λ_A a factor which is close to unity[36,37] $[\cdot,\cdot]$ the commutator and $\{\cdot,\cdot\}_+$ the anticommutator. While $\hat{h}_{\mathrm{pv}}^{(2)}(i)$ and $\hat{h}_{\mathrm{pv}}^{(3)}(i)$ are important for parity violating effects in NMR spectra[17,38,39] they can usually be ignored when calculating parity violating potentials of chiral molecules. Since $\hat{h}_{\mathrm{pv}}^{(2)}(i)$ and $\hat{h}_{\mathrm{pv}}^{(3)}(i)$ vanish naturally when $\sin^2\theta_w=0.25$, we have used this theoretical value for most of the calculations within this work. For comparison with future experiments, however, in selected cases we applied the current experimental value of $\sin^2\theta_w=0.2319$, the quantitative differences between the two sets of calculations being small.

As has been frequently pointed out, the expectation value of $\hat{H}_{\mathrm{pv}}$ for a nondegenerate singlet eigenstate $|0\rangle$ of a purely electrostatic Hamiltonian $\hat{H}_0$ vanishes. Therefore, one has to consider additional terms in order to obtain nonvanishing parity violating potentials. These additional terms can either be explicitly included in the molecular Hamiltonian or estimated via perturbation theory. Usually, the spin–orbit interaction is expected to account for the strongest coupling effects and thus for the largest first-order correction to the molecular wave function. The operator (in atomic units) for this interaction reads in the Breit–Pauli form as[40–43]

$$\hat{H}_{\mathrm{SO}}=\frac{\alpha^2}{2}\left[\sum_{i=1}^{n}\sum_{A=1}^{N}Z_A\frac{\hat{\vec{l}}_{i,A}\cdot\hat{\vec{s}}_i}{|\vec{r}_A-\vec{r}_i|^3}+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\hat{\vec{l}}_{i,j}(\hat{\vec{s}}_i+2\hat{\vec{s}}_j)}{|\vec{r}_i-\vec{r}_j|^3}\right],\tag{2}$$

where $\hat{\vec{l}}_{i,\mu}$ refers to the orbital angular momentum of electron i with respect to the position of particle μ. In second-order perturbation theory the operators $\hat{H}_{\mathrm{pv}}$ and $\hat{H}_{\mathrm{SO}}$ give rise to a nonvanishing parity violating potential according to[7,15,22]

$$E_{\mathrm{pv}}=2\,\mathrm{Re}\left\{\sum_j\frac{\langle0|\hat{H}_{\mathrm{pv}}|\Psi_j\rangle\langle\Psi_j|\hat{H}_{\mathrm{SO}}|0\rangle}{E_0-E_j}\right\},\tag{3}$$

where $|0\rangle$ denotes the reference state of interest, E_0 the corresponding energy and $|\Psi_j\rangle$ the jth excited state with energy E_j. In the following discussion we will restrict ourselves to a singlet reference state. This allows us to save computational work because $\hat{H}_{\mathrm{pv}}$ and $\hat{H}_{\mathrm{SO}}$ couple a singlet state only to the triplet manifold. Therefore, we can omit all nontriplet states from the summation in Eq. (3).

If we make additional assumptions about the nature of the reference and the triplet states, we can rewrite the general equation (3) in a more explicit form. Within the SDE-RHF approach, for instance, the reference state is assumed to be the restricted Hartree–Fock ground state $|0_{\mathrm{RHF}}\rangle$, while the manifold of the excited triplet states is approximated by singly excited Slater determinants $|\Phi_{i\to j}\rangle$. Taking into account only one-electron terms of the spin–orbit coupling operator $\hat{H}_{\mathrm{SO}}$, that is $\hat{H}_{\mathrm{SO}}=\Sigma_{i=1}^{n}\hat{h}_{\mathrm{SO}}(i)=\Sigma_{i=1}^{n}\Sigma_{A=1}^{N}f_A(\vec{r}_i-\vec{r}_A)\hat{\vec{l}}_{i,A}\cdot\hat{\vec{s}}_i$, the parity violating potential has the following form:[14,15,44]

$$\begin{aligned}E_{\mathrm{pv}}=&\frac{G_F\alpha}{\sqrt{2}}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}\sum_{A=1}^{N}\sum_{B=1}^{N}Q_W(A)\\&\times\frac{\langle\phi_i|\{\hat{\vec{p}}_1,\delta^3(\vec{r}_1-\vec{r}_A)\}_+|\phi_j\rangle\langle\phi_j|f_B(\vec{r}_1-\vec{r}_B)\hat{\vec{l}}_{1,B}|\phi_i\rangle}{\epsilon_i-\epsilon_j+J_{ij}}.\end{aligned}\tag{4}$$

Here $|\phi_i\rangle$ and $|\phi_j\rangle$ represent occupied and virtual spatial molecular orbitals with orbital energies ϵ_i and ϵ_j, respectively. In the pioneering work of Hegstrom *et al.*[15] and in some later calculations the denominator of Eq. (4) has been approximated solely by the orbital energy differences, whereas an exact treatment requires the knowledge of the Coulomb integral J_{ij} [or alternatively the use of accurate energies E_0-E_j in Eq. (3)].

While the SDE-RHF method has the merit of simplicity, it suffers from the usually unsatisfactory description of electronically excited states with a single-determinant wave function.

The main goal of the CIS-RHF approach[21,22] is to improve the description of the excited triplet states entering the sum in Eq. (3). While this method still relies on the RHF ground state $|0_{\mathrm{RHF}}\rangle$, the excited triplet states are now the eigenstates of a configuration interaction calculation using singly excited determinants as basis functions. The parity violating potential then reads[22]

$$E_{\mathrm{pv}}=\frac{G_F\alpha}{\sqrt{2}}\sum_n\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}\sum_k^{\mathrm{occ}}\sum_l^{\mathrm{unocc}}C^n_{i\to j}(M_S)\times C^n_{k\to l}(M_S)\sum_{A=1}^{N}\sum_{B=1}^{N}Q_W(A)\times\frac{\langle\phi_i|\{\hat{\vec{p}}_1,\delta^3(\vec{r}_1-\vec{r}_A)\}_+|\phi_j\rangle\langle\phi_j|f_B(\vec{r}_1-\vec{r}_B)\hat{\vec{l}}_{1,B}|\phi_i\rangle}{E_0-E_n},\tag{5}$$

where $|\Phi_{i\to j}\rangle$ is a singly excited triplet configuration state function with quantum number M_S of the z-component of the electron spin and where $C^n_{i\to j}(M_S)$ is the coefficient of this configuration state function entering the electronic triplet state $|\Psi_n\rangle$ which corresponds to the same value of M_S. Since summation over the three triplet components has been performed when deriving Eq. (5), we are free to choose the coefficients of the configuration state functions for one of the M_S values, that is either -1, 0 or $+1$.

Obviously, this approach is superior to the SDE-RHF due to the improved description of the excited triplet states. However, one of its drawbacks is that a large number of electronically excited states is required since the sum-over-states expansion converges very slowly.[21,22] Also, in quite a few cases the single-determinant description accounts for only a qualitative picture of the reference state and fails completely for the limiting case of a biradical compound. Therefore, the SDE-RHF and CIS-RHF approaches suffer from the deficiencies of the RHF approximation for the reference state as has been demonstrated in Ref. 22 for twisted ethylene. Both difficulties can be avoided with the conceptually different multiconfiguration linear response approach,[45] which we use in this paper for the calculation of parity violating potentials.

B. Multiconfiguration linear response (MCLR) approach to electroweak molecular quantum chemistry

In the framework of response theory the parity violating potential E_{pv} is given by the linear response function (denoted by $\langle\langle .;.\rangle\rangle_{\omega_1}$)

$$E_{\mathrm{pv}}=\langle\langle\hat{H}_{\mathrm{SO}};\hat{H}_{\mathrm{pv}}\rangle\rangle_{\omega_1=0}=\langle\langle\hat{H}_{\mathrm{pv}};\hat{H}_{\mathrm{SO}}\rangle\rangle_{\omega_1=0}\tag{6}$$

which is itself defined via the time evolution of the expectation value of the operator on the left-hand side of the semicolon, according to

$$A_{\mathrm{av}}(t)=\langle 0|\hat{A}|0\rangle+\int_{-\infty}^{\infty}\langle\langle\hat{A};\hat{B}^{\omega_1}\rangle\rangle_{\omega_1}\exp[-i\omega_1 t]\,d\omega_1+\text{higher order terms},\tag{7}$$

where $A_{\mathrm{av}}(t)$ is the time development of the average value of the operator $\hat{A}$ and $\hat{B}^{\omega_1}$ the interaction operator in the frequency domain.

In the MCSCF approximation the reference state $|0\rangle$, which is not necessarily the electronic ground state, is expanded in a basis of configuration state functions (CSF) $|\Phi_m\rangle$ according to

$$|0\rangle=\sum_m C^0_m|\Phi_m\rangle\tag{8}$$

with each CSF being a linear combination of Slater determinants.

As in common MCSCF calculations the response equations are solved in the subspace generated by the orbital excitation and de-excitation operators $\hat{q}_i^+$ and $\hat{q}_i$ with $\hat{q}_i^+=\hat{a}_p^+\hat{a}_q$, $p>q$ and the state transfer operators $\hat{R}_i^+$ and $\hat{R}_i$ with $\hat{R}_i^+=|i\rangle\langle 0|$ and $\{|i\rangle\}$ denoting the orthogonal complement of the reference state $|0\rangle$ (see Ref. 45).

In our case, where we have static perturbations ($\omega_1=0$), a singlet reference state and operators inducing a coupling to the triplet manifold (see Refs. 46–48 for this special type of operator), the general equation (6.7) of Ref. 45 reads

$$E_{\mathrm{pv}}=\langle\langle\hat{H}_{\mathrm{pv}};\hat{H}_{\mathrm{SO}}\rangle\rangle_0=\vec{H}^{[1]\dagger}_{\mathrm{pv}}(\mathbf{E}^{[2]})^{-1}\vec{H}^{[1]}_{\mathrm{SO}}\tag{9}$$

with gradient-type vectors with elements

$$H^{[1]}_{\mathrm{pv},i}=\langle 0|[\hat{T}_i^+,\hat{H}_{\mathrm{pv}}]|0\rangle,\tag{10}$$

$$H^{[1]}_{\mathrm{SO},i}=\langle 0|[\hat{T}_i^+,\hat{H}_{\mathrm{SO}}]|0\rangle,\tag{11}$$

and the generalized Hessian matrix[45]

$$\mathbf{E}^{[2]}=\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B}^* & \mathbf{A}^*\end{pmatrix},\tag{12}$$

where

$$\mathbf{A}=\begin{pmatrix}\langle 0|[\hat{q}_j,[\hat{H}_0,\hat{q}_l^+]]|0\rangle & \langle 0|[[\hat{q}_j,\hat{H}_0],\hat{R}_l^+]|0\rangle\\ \langle 0|[\hat{R}_j,[\hat{H}_0,\hat{q}_l^+]]|0\rangle & \langle 0|[\hat{R}_j,[\hat{H}_0,\hat{R}_l^+]]|0\rangle\end{pmatrix},\tag{13}$$

$$\mathbf{B}=\begin{pmatrix}\langle 0|[\hat{q}_j,[\hat{H}_0,\hat{q}_l]]|0\rangle & \langle 0|[[\hat{q}_j,\hat{H}_0],\hat{R}_l]|0\rangle\\ \langle 0|[\hat{R}_j,[\hat{H}_0,\hat{q}_l]]|0\rangle & \langle 0|[\hat{R}_j,[\hat{H}_0,\hat{R}_l]]|0\rangle\end{pmatrix}\tag{14}$$

using the vector operator $\hat{\vec{T}}=(\hat{\vec{q}}^+,\hat{\vec{R}}^+,\hat{\vec{q}},\hat{\vec{R}})$ with elements $\hat{T}_i$ as a short-hand notation.[45] $\hat{\vec{q}}^+$ and $\hat{\vec{q}}$ are in our case triplet excitation and de-excitation operators and $\hat{\vec{R}}^+$, $\hat{\vec{R}}$ are singlet–triplet state transfer operators (see Refs. 46–48).

Equation (9) can be solved in a two-step procedure.[45] First we solve the linear response equation

$$\mathbf{E}^{[2]}\vec{N}=\vec{H}^{[1]}_{\mathrm{SO}}\tag{15}$$

for the vector $\vec{N}$ carrying the orbital excitation and configuration amplitudes. Then this vector is contracted with $\vec{H}^{[1]}_{\mathrm{pv}}$ to yield

$$\langle\langle\hat{H}_{\mathrm{pv}};\hat{H}_{\mathrm{SO}}\rangle\rangle_{\omega_1=0}=\vec{H}^{[1]\dagger}_{\mathrm{pv}}\vec{N}\tag{16}$$

which is the quantity of interest. The linear response equations can be solved in a direct iterative manner without explicitly constructing the Hessian matrix.[45,46,49]

The structure of the gradient-type vector $\vec{H}^{[1]}_{\mathrm{pv}}$ is equivalent to the one-electron part of $\vec{H}^{[1]}_{\mathrm{SO}}$, which has been described in Refs. 46 and 47. In second-quantization language $\vec{H}_{\mathrm{pv}}$ reads

$$\hat{H}_{\mathrm{pv}}=\sum_{i}\sum_{j}\vec{h}_{ij}\cdot\hat{\vec{s}}_{ij} \tag{17}$$

with i and j representing molecular orbital indices and

$$\vec{h}_{ij}=\frac{G_F\alpha}{2\sqrt{2}}\sum_{A=1}^{N}Q_W(A)\langle\phi_i|\{\hat{\vec{p}}_1,\delta^3(\vec{r}_1-\vec{r}_A)\}_+|\phi_j\rangle, \tag{18}$$

$$\hat{s}^x_{ij}=\frac{\hat{a}^+_{i\alpha}\hat{a}_{j\beta}+\hat{a}^+_{i\beta}\hat{a}_{j\alpha}}{2}, \tag{19}$$

$$\hat{s}^y_{ij}=\frac{\hat{a}^+_{i\alpha}\hat{a}_{j\beta}-\hat{a}^+_{i\beta}\hat{a}_{j\alpha}}{2i}, \tag{20}$$

$$\hat{s}^z_{ij}=\frac{\hat{a}^+_{i\alpha}\hat{a}_{j\alpha}-\hat{a}^+_{i\beta}\hat{a}_{j\beta}}{2}. \tag{21}$$

The spin-part of the parity violating operator is identical to the spin-part of the one-electron term of $\hat{H}_{\mathrm{SO}}$ and can therefore be treated in a similar manner—except, of course, for the modified spatial part. The Dalton program[50] is capable to compute second-order energy corrections due to spin–orbit coupling in the multiconfiguration linear response approximation and two of its special cases, namely the random phase approximation (RPA), where only orbital excitation and de-excitation operators are involved, and the configuration interaction approach, where only the state-transfer operators are included.

Therefore, we modified the Dalton program in order to compute the parity violating potential E_{pv} in the MCLR approximation. Since within the program $\hat{H}_{\mathrm{pv}}$ can be treated on the same footing as the one-electron part of $\hat{H}_{\mathrm{SO}}$, the only necessary step was to allow for the computation of the spatial part of the matrix elements of $\hat{H}_{\mathrm{pv}}$ in the atomic orbital basis $\{|\chi_\mu\rangle\}$. Essentially these matrix elements are

$$\begin{aligned}&\langle\chi_\mu|\boldsymbol{\nabla}_1\delta^3(\vec{r}_1-\vec{r}_C)+\delta^3(\vec{r}_1-\vec{r}_C)\boldsymbol{\nabla}_1|\chi_\nu\rangle\\&\quad=\langle\chi_\mu|\delta^3(\vec{r}_1-\vec{r}_C)|\boldsymbol{\nabla}_1\chi_\nu\rangle-\langle\boldsymbol{\nabla}_1\chi_\mu|\delta^3(\vec{r}_1-\vec{r}_C)|\chi_\nu\rangle,\end{aligned} \tag{22}$$

where $\vec{r}_1$ denotes the position vector of electron 1 with components x_1, y_1, z_1,$\boldsymbol{\nabla}_1$ is the corresponding Nabla operator, and $\vec{r}_C$ the position vector of nucleus C. When the spatial atomic orbitals are expanded in terms of (unnormalized) Gaussians

$$\begin{aligned}G_{\vec{i}}(\vec{r}_1,a,\vec{r}_A)&=G_{i_x}(x_1,a,x_A)G_{i_y}(y_1,a,y_A)G_{i_z}(z_1,a,z_A)\\&=x_{1A}^{i_x}y_{1A}^{i_y}z_{1A}^{i_z}\exp[-a(x_{1A}^2+y_{1A}^2+z_{1A}^2)],\end{aligned} \tag{23}$$

where we used $x_{1A}=x_1-x_A$ and similar expressions for the y- and z-components, then the x-component of the integral given in Eq. (22) is

$$\begin{aligned}&\int G_{\vec{i}}(\vec{r}_1,a,\vec{r}_A)\,\delta^3(\vec{r}_{1C})\,\frac{\partial G_{\vec{j}}(\vec{r}_1,b,\vec{r}_B)}{\partial x_1}\,d\vec{r}_1\\&\quad-\int\frac{\partial G_{\vec{i}}(\vec{r}_1,a,\vec{r}_A)}{\partial x_1}\,\delta^3(\vec{r}_{1C})G_{\vec{j}}(\vec{r}_1,b,\vec{r}_B)d\vec{r}_1\\&\quad=[x_{CA}^{i_x}(j_x x_{CB}^{j_x-1}-2bx_{CB}^{j_x+1})-(i_x x_{CA}^{i_x-1}-2ax_{CA}^{i_x+1})x_{CB}^{j_x}]\\&\qquad\times y_{CA}^{i_y}y_{CB}^{j_y}z_{CA}^{i_z}z_{CB}^{i_z}\exp[-pr_{CP}^2]\end{aligned} \tag{24}$$

with $x_{CA}=x_C-x_A$ and similar expressions for other components as well as $p=a+b$ and $P=[(a\vec{r}_A+b\vec{r}_B)/p]$ as a short-hand notation. Likewise the remaining components of the spatial part of the parity violating operator can be computed.

As an alternative route we used the McMurchie–Davidson scheme[51] for the computation of the spatial part of the matrix elements of $\hat{H}_{\mathrm{pv}}$, since this scheme is frequently applied in the Dalton program for the computation of other property integrals. The central concept of this method is to expand the product of two Gaussians (the so-called overlap distribution) in terms of Hermite functions according to

$$\begin{aligned}\Omega_{i_xj_x}&=G_{i_x}(x_1,a,x_A)G_{j_x}(x_1,b,x_B)\\&=\sum_{t_x=0}^{i_x+j_x}E^{t_x}_{i_xj_x}\Lambda_{t_x}(x_1,p,x_P)\end{aligned} \tag{25}$$

and analogue equations for the y- and z-components, where $\Lambda_{t_x}(x_1,p,x_P)=(\partial/\partial x_P)^{t_x}\exp[-px_P^2]$ and where the $E^{t_x}_{i_xj_x}$ are expansion coefficients, which can be computed via recurrence relations.[51]

Due to the equality $-(\partial/\partial x_1)G_{j_x}(x_1,b,x_B)=(\partial/\partial x_B)G_{j_x}(x_1,b,x_B)$ we can write

$$\begin{aligned}\Omega_{i_xj'_x}&=-G_{i_x}(x_1,a,x_A)\frac{\partial}{\partial x_1}G_{j_x}(x_1,b,x_B)\\&=\frac{\partial\Omega_{i_xj_x}}{\partial x_B}=\sum_{t_x=0}^{i_x+j_x+1}E^{t_x}_{i_xj'_x}\Lambda_{t_x}(x_1,p,x_P),\end{aligned} \tag{26}$$

where $E^{t_x}_{i_xj'_x}=2bE^{t_x}_{i_xj_x+1}-j_xE^{t_x}_{i_xj_x-1}$ and in analogy $E^{t_x}_{i'_xj_x}=2aE^{t_x}_{i_x+1j_x}-i_xE^{t_x}_{i_x-1j_x}$. Then we can write the left-hand side of Eq. (24) as

$$\begin{aligned}&-\int\frac{\partial\Omega_{\vec{i}\vec{j}}}{\partial x_B}\,\delta(\vec{r}_{1C})d\vec{r}_1+\int\frac{\partial\Omega_{\vec{i}\vec{j}}}{\partial x_A}\,\delta(\vec{r}_{1C})d\vec{r}_1\\&\quad=\sum_{t_x=0}^{i_x+j_x+1}\sum_{t_y=0}^{i_y+j_y}\sum_{t_z=0}^{i_z+j_z}(-E^{t_x}_{i_xj'_x}+E^{t_x}_{i'_xj_x})E^{t_y}_{i_yj_y}E^{t_z}_{i_zj_z}\\&\qquad\times\int\Lambda_{t_x}\delta(x_{1C})dx_1\int\Lambda_{t_y}\delta(y_{1C})dy_1\int\Lambda_{t_z}\delta(z_{1C})dz_1\\&\quad=\sum_{t_x=0}^{i_x+j_x+1}\sum_{t_y=0}^{i_y+j_y}\sum_{t_z=0}^{i_z+j_z}(E^{t_x}_{i'_xj_x}-E^{t_x}_{i_xj'_x})E^{t_y}_{i_yj_y}E^{t_z}_{i_zj_z}\\&\qquad\times\Lambda_{t_x}(x_C,p,x_P)\Lambda_{t_y}(y_C,p,y_P)\Lambda_{t_z}(z_C,p,z_P).\end{aligned} \tag{27}$$

Since the Hermite functions $\Lambda_t(x_1,p,x_P)$ are related to the Hermite polynomials $H_t(\xi)$ via

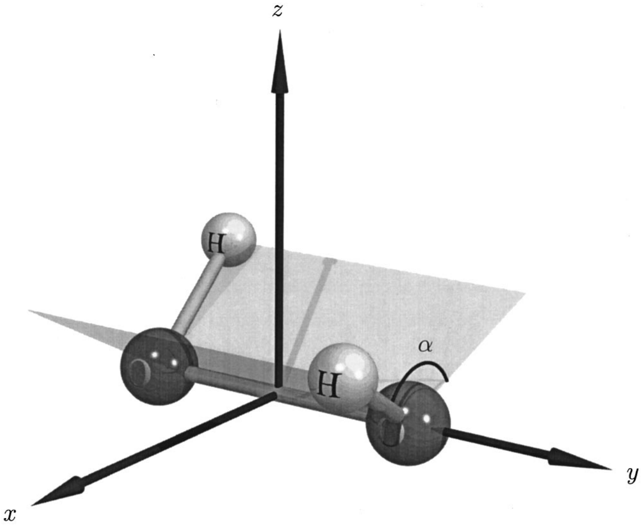

FIG. 1. Structure and orientation of the hydrogen peroxide enantiomer used in this study (P-enantiomer, see Ref. 65).

TABLE I. Parity violating potentials as a function of torsional angle in hydrogen peroxide for various methods (see text for acronyms) using 6-31 G as basis set.

		$E_{\mathrm{pv}}/(10^{-20}E_h)$				
Method	Basis set	30°	60°	90°	120°	150°
RPA	6-31G	−35.20	−30.37	6.08	38.74	36.88
RPA[a]	6-31G	−32.65	−28.17	5.64	35.94	34.21
RPA[b]	6-31G	−54.12	−47.29	7.79	57.49	55.19
CIS	6-31G	−39.52	−32.35	11.51	50.42	47.10
CIS[a]	6-31G	−36.66	−30.00	10.67	46.76	43.69
CIS[c]	6-31G	−42.98	−36.43	11.49	51.79	48.99
CISD	6-31G	−7.83	−6.37	2.38	9.94	9.05
CISDT	6-31G	−32.68	−26.36	9.83	41.87	39.12
CISDTQ(1sf)	6-31G	−28.22	−22.70	8.67	36.35	33.84
CASSCF-LR	6-31G	−30.67	−24.97	9.11	39.32	36.61
CASSCF-LR[a]	6-31G	−28.45	−23.17	8.45	36.47	33.96
RASSCF+1-LR	6-31G	−30.91	−24.71	10.87	42.20	38.95
RASCIS	6-31G	−28.41	−24.20	5.49	31.79	29.99
RASCISD	6-31G	−18.25	−15.11	4.98	22.64	20.93
RASCISDT	6-31G	−20.93	−16.96	6.28	26.45	24.31
RASCISDTQ	6-31G	−20.84	−16.86	6.32	26.41	24.26
RASCI(full)	6-31G	−20.85	−16.86	6.32	26.43	24.27

[a] Experimental $\sin^2\theta_w$,

[b] Reference 31.

[c] References 21 and 22.

$$\Lambda_t(x_1,p,x_P)=a^{t/2}H_t(a^{1/2}x_{1P})\exp[-ax_{1P}^2] \qquad (28)$$

the well-known recurrence relations of the Hermite polynomials can be used in oder to compute the Hermite functions.

In the following section we present the results obtained for parity violating potentials in hydrogen peroxide and ethylene using our modified version of the Dalton program.

III. RESULTS AND DISCUSSION

A. Hydrogen peroxide

Hydrogen peroxide has a chiral equilibrium geometry with a low barrier for the stereomutation interconverting the two enantiomeric structures. Theoretical investigations revealed that extensive basis sets as well as highly correlated electronic wave functions are required in order to obtain proper structural parameters for the chiral equilibrium geometries and reliable barrier heights for their interconversion (see Refs. 52 and 53 and references cited therein).

Nevertheless, previous nonrelativistic calculations of the parity violating potential in hydrogen peroxide[16,21,22,31] used the SDE-RHF, CIS-RHF or the RP approximations, which still base on an RHF ground state picture. One is tempted to argue, that $\hat{H}_{\mathrm{pv}}$ and $\hat{H}_{\mathrm{SO}}$ depend essentially on the character of the wave functions in the vicinity of the nucleus and less on the diffuse part responsible for the interaction between the nonbonding orbitals at the oxygen atoms, which requires correlated wave functions to be described properly. Therefore, one would expect that comparatively low-level approaches may provide a reasonable estimate of the parity violating potential, but this needs to be confirmed explicitly. The MCLR approach enables us to judge, whether previous approximations are justified. In order to do so, we first calculated the parity violating potential with different methods applying the relatively small 6-31G basis set. Then we studied the basis set dependence of the parity violating potential, addressing especially the question, whether tight, diffuse or polarization functions are required for a proper description of E_{pv}. We further investigated the interplay of the one- and two-electron spin–orbit terms.

For comparison with previous studies[16,21,22,31] we used the same geometry (O–O and H–O bond lengths of 149 pm and 97 pm, respectively, as well as an H–O–O angle of 100.0°) and varied the dihedral angle α between 0 and 180 degrees for the P-enantiomer shown in Fig. 1 (M-enantiomer from 180° to 360°).

Table I shows the results obtained for the various methods using the 6-31G basis set. The data for the CIS method is essentially the same as in Ref. 22. Differences are due to the one-center approximation as well as the effective one-electron operator for the spin–orbit coupling term used there. The RPA values, however, deviate significantly from those given in Ref. 31. This can be attributed to the bare nucleus potential for the one-electron part of the spin–orbit operator used in Ref. 31, where the two-electron terms were neglected. As is well known from spin–orbit coupling calculations (see for instance Refs. 47 and 54) and as has been explicitly demonstrated in Ref. 19 for the parity violating potential, the two-electron terms of the spin–orbit coupling operator are essential if a bare nucleus potential is used. However, one can to some extent compensate the influence of the two-electron terms with an effective screened nuclear potential Z_{eff} which serves as an adjustable parameter for the calculation. For oxygen $Z_{\mathrm{eff}}=0.66Z$ is a commonly chosen parameter, and consequently the RPA results for E_{pv} of Ref. 31 are too large by a factor of approximately 1.5.

Inspection of the results obtained for the various methods using the theoretical and the experimental value of $\sin^2\theta_w$ shows that a simple scaling with the factor 0.2319/0.25 of the data based on the theoretical value for the Weinberg angle θ_w yields data almost exactly coinciding with the

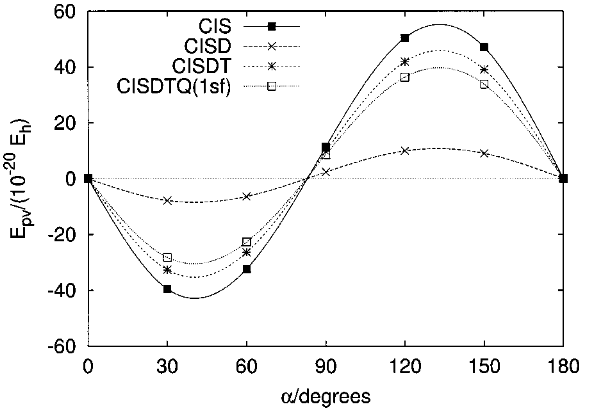

FIG. 2. E_{pv} in hydrogen peroxide for the CI method with various excitation levels using $\sin^2\theta_w=0.25$ (see text for acronyms).

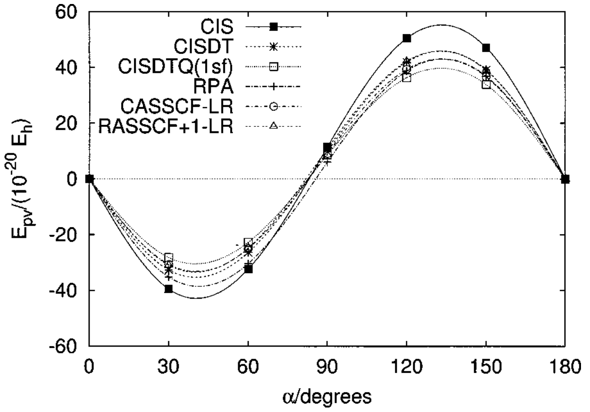

FIG. 4. E_{pv} in hydrogen peroxide for various methods using $\sin^2\theta_w=0.25$ (see text for acronyms).

parity violation potentials computed for the experimental value of θ_w. According to Eqs. (4) and (5), scaling the factor $\sin^2\theta_w$ would be an exact procedure, if the number of neutrons and protons were the same for all nuclei. This would be the case for D_2O_2.

The results for the CILR method using excitation schemes from CIS to CISDTQ(lsf) (for the latter we kept the 1s orbitals of the oxygen atoms frozen) are displayed in Fig. 2. While the CIS estimates seem to be a reasonable approximation to the CISDT and CISDTQ(lsf) results, the CISD values account only for roughly one fourth of the CISDTQ(lsf) values.

We establish a similar trend in calculations where we have only allowed for excitations within an active space composed of occupied RHF orbitals and virtual valence orbitals. For this kind of restricted active space configuration interaction calculation (RASCI) we observe again, that the RASCISD values are too low compared to those of the RASCISDT and the RASCI(full) (see Fig. 3). Nonetheless, here the effect is less pronounced. It turns out for the CI and for the RASCI methods as well, that the absolute value of the parity violating potential at a given dihedral angle exhibits an oscillating behavior with respect to the excitation levels. While the series of odd excitation levels (CIS, CISDT and so forth) seems to asymptotically approach the full CI value from above, the even excitation levels (CISD, CISDTQ and so forth) approach this value from below. We therefore expect the value of the parity violating potential of a full CI expansion for this basis set to be bracketed by the interval given by the CISDT and CISDTQ(lsf) values.

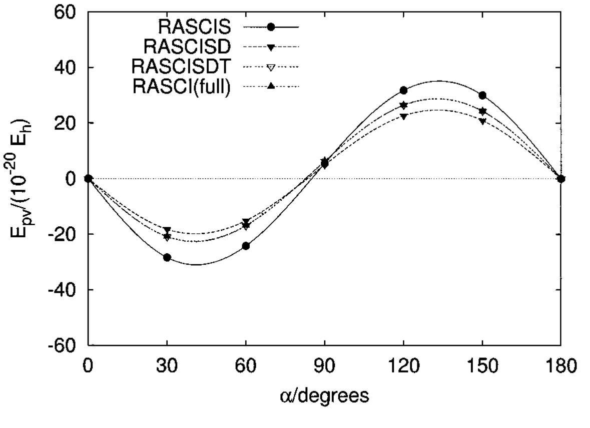

FIG. 3. E_{pv} in hydrogen peroxide for the restricted active space CI method with various excitation levels using $\sin^2\theta_w=0.25$ (see text for acronyms).

In Fig. 4 we compare the results of the CIS-RHF and RPA methods already applied in previous work with the results from a CISDT and CISDTQ(lsf) calculation, from a complete active space self-consistent-field–linear response (CASSCF-LR) calculation using an active space including the valence orbitals as well as the oxygen 1s orbitals, and finally from a restricted active space self-consistent-field computation where we furthermore allowed for excitations of one electron from the active space to all the secondary orbitals (RASSCF+1-LR).

For all geometries of hydrogen peroxide studied here the results of the CASSCF-LR calculations fall into the interval where we expect the full CI value. At small dihedral angles the high-level RASSCF+1-LR method yields essentially the same parity violating potentials as CASSCF-LR, whereas at large dihedral angles the RASSCF+1-LR values almost coincide with the results of the CISDT calculation. RPA yields for large dihedral angles basically the same parity violating potentials as CASSCF-LR, while at small angles this method gives rise to values which are slightly too large in magnitude. CIS tends to give values that are too large by 20–40 percent.

Inspection of the CAS wave function shows that for smaller dihedral angles the HF ground state determinant becomes slightly less dominant and doubly and higher excited configurations become more important in order to describe the increasing interaction between the lone-pairs of the oxygen atoms. Consequently the CIS and RPA method are less reliable for these geometries, while both methods work well qualitatively, since mainly singly excited configurations contribute to the parity violating potential, predominantly configurations involving the nonoccupied B-symmetric molecular orbital, which is essentially described by the $2p_y-2s$ hybrid orbitals of the oxygen pointing away from the O–O bond. The variety of CI expansions employed in this study revealed that the parity violating potential depends on the interplay of even and odd excitation levels. Since RPA—in contrast to CIS—includes some coupling to doubly excited

TABLE II. Basis set dependence of E_{pv} in hydrogen peroxide for CASSCF-LR and RPA.

Method	Basis set	$E_{\mathrm{pv}}/(10^{-20}E_h)$				
		30°	60°	90°	120°	150°
CASSCF-LR	6-31G	−30.67	−24.97	9.11	39.32	36.61
CASSCF-LR	cc-pVDZ	−29.86	−25.62	7.85	38.87	36.87
CASSCF-LR	aug-cc-pVDZ	−29.01	−25.42	6.93	37.65	36.15
CASSCF-LR	aug-cc-pCVDZ	−32.48	−28.60	7.30	41.49	39.94
CASSCF-LR	cc-pVTZ	−35.66	−31.11	8.30	45.16	43.18
CASSCF-LR[a]	cc-pVTZ	−33.08	−28.86	7.70	41.89	40.05
CASSCF-LR	aug-cc-pVTZ	−34.87	−30.90	7.74	44.48	42.70
CASSCF-LR	aug-cc-pCVTZ	−36.35	−32.17	7.91	46.04	44.32
RPA	6-31G	−35.20	−30.37	6.08	38.74	36.88
RPA	cc-pVDZ	−33.48	−29.71	5.88	38.93	37.37
RPA	aug-cc-pVDZ	−33.05	−29.74	5.29	38.44	37.30
RPA	aug-cc-pCVDZ	−37.29	−33.67	5.53	42.66	41.53
RPA	cc-pVTZ	−41.73	−37.38	6.34	47.14	45.64
RPA[a]	cc-pVTZ	−38.70	−34.67	5.88	43.73	42.34
RPA	aug-cc-pVTZ	−41.04	−37.28	5.91	46.80	45.42
RPA	aug-cc-pCVTZ	−42.45	−38.48	6.03	48.14	46.84

[a] Experimental $\sin^2\theta_w$.

states [through the matrix elements $\mathbf{B}_{11}$ in Eq. (14)], this method yields quite good values for the parity violating potential at larger dihedral angles.

However, these trends obtained with the 6-31G basis set may change with increasing quality of the atomic basis set. In order to investigate the basis set convergence, we report in Table II RPA and CASSCF-LR calculations using various samples from the series of the correlation consistent basis sets introduced by Dunning.[55] The two-electron spin–orbit integrals are the limiting factor for our basis set study, since their number is approximately 6 times that of the two electron-coulomb integrals. We notice that augmentation of the basis set with diffuse functions has comparatively little effect on the parity violating potential compared to the more pronounced influence of additional tight functions on the result for E_{pv}.

In order to allow for a larger basis set expansion we analyzed the one- and two-electron spin–orbit contributions to the parity violating potential and tried to find an effective nuclear charge for the one-electron spin–orbit operator

TABLE III. One-electron $(1e)$ versus two-electron $(2e)$ contribution of $\hat{H}_{\mathrm{SO}}$ to E_{pv} and resulting scaling factor f in hydrogen peroxide for various basis sets.

Method	Basis set		$E_{\mathrm{pv}}/(10^{-20}E_h)$			
			30°	60°	120°	150°
CASSCF-LR	cc-pVDZ	$1e$	−45.66	−39.53	58.16	55.42
		$2e$	15.80	13.91	−19.29	−18.55
		f	0.654	0.648	0.668	0.665
	aug-cc-pVDZ	$1e$	−44.24	−39.09	56.43	54.42
		$2e$	15.23	13.67	−18.78	−18.26
		f	0.656	0.650	0.667	0.664
	aug-cc-pCVDZ	$1e$	−49.39	−43.77	62.17	60.09
		$2e$	16.92	15.17	−20.68	−20.15
		f	0.658	0.653	0.667	0.665
	cc-pVTZ	$1e$	−53.75	−47.19	67.01	64.42
		$2e$	18.09	16.08	−21.85	−21.24
		f	0.663	0.659	0.674	0.670
	cc-pVTZ[a]	$1e$	−49.81	−43.71	62.18	59.76
		$2e$	16.74	14.86	−20.29	−19.71
		f	0.664	0.660	0.674	0.670
	aug-cc-pVTZ	$1e$	−52.52	−46.86	66.01	63.64
		$2e$	17.64	15.96	−21.53	−20.94
		f	0.664	0.659	0.674	0.671
RPA	cc-pVDZ	$1e$	−51.23	−45.96	57.78	55.85
		$2e$	17.76	16.25	−18.86	−18.48
		f	0.653	0.646	0.674	0.669
	aug-cc-pVDZ	$1e$	−50.48	−45.88	57.22	55.88
		$2e$	17.43	16.14	−18.78	−18.58
		f	0.655	0.648	0.672	0.667
	aug-cc-pCVDZ	$1e$	−56.80	−51.70	63.53	62.19
		$2e$	19.51	18.04	−20.87	−20.66
		f	0.656	0.651	0.672	0.668
	cc-pVTZ	$1e$	−62.93	−56.85	69.43	67.70
		$2e$	21.21	19.47	−22.29	−22.06
		f	0.663	0.657	0.679	0.674
	cc-pVTZ[a]	$1e$	−58.37	−52.73	64.40	62.80
		$2e$	19.67	18.06	−20.67	−20.46
		f	0.663	0.657	0.679	0.674
	aug-cc-pVTZ	$1e$	−61.88	−56.68	68.93	67.32
		$2e$	20.85	19.40	−22.13	−21.90
		f	0.663	0.658	0.679	0.675

[a] Experimental $\sin^2\theta_w$.

TABLE IV. Parity violating potentials in hydrogen peroxide obtained using a one- and two-electron $(1e+2e)$ as well as an effective one-electron (eff) spin–orbit coupling operator.

Method	Basis set	$E_{\mathrm{pv}}/(10^{-20}E_h)$ 30°	60°	90°	120°	150°
CASSCF-LR $(1e+2e)$	cc-pVDZ	−29.86	−25.62	7.85	38.87	36.87
CASSCF-LR (eff)	cc-pVDZ	−30.45	−26.39	7.33	38.72	36.92
CASSCF-LR $(1e+2e)$	cc-pVTZ	−35.66	−31.11	8.30	45.16	43.18
CASSCF-LR (eff)	cc-pVTZ	−35.84	−31.50	7.73	44.64	42.92
CASSCF-LR (eff)	cc-pVQZ	−40.16	−35.85	8.15	50.15	48.39
RPA $(1e+2e)$	cc-pVDZ	−33.48	−29.71	5.88	38.93	37.37
RPA (eff)	cc-pVDZ	−34.16	−30.66	5.10	38.50	37.22
RPA $(1e+2e)$	cc-pVTZ	−41.73	−37.38	6.34	47.14	45.64
RPA (eff)	cc-pVTZ	−41.94	−37.90	5.50	46.28	45.14
RPA (eff)	cc-pVQZ	−46.86	−42.87	5.83	52.11	50.96
RPA (eff)	cc-pV5Z	−51.54	−47.12	6.46	57.45	56.16

which compensates the effect of the two-electron part. The results are reported in Table III. An effective nuclear charge of $5.304|e_0|$ for oxygen gives good overall agreement between calculations including one- and two-electron terms and those using the effective one-electron spin–orbit operator. With this value we were able to apply larger basis sets for which the results are given in Table IV. The results show that even for the largest basis set used here, there is still a small, but significant increase of E_{pv}. Indeed, changes with basis set of the order of 5–20 percent are about as important as the differences arising from methods of different quality (CIS, RPA, CASSCF-LR, etc.)

We may conclude, for the moment, that for the torsional motion in hydrogen peroxide the CIS method and the RP approximation both provide reasonable estimates for the parity violating potential obtained with the CASSCF-LR approach. The magnitude of the CIS results tends to be 20–40 percent too large while the RP approximation performs somewhat better with slight deviations of no more than 20 percent at small dihedral angles. Apart from CISD, all the methods applied here provide similar results within a factor of 3. It thus seems that the order of magnitude of the parity violating potential in hydrogen peroxide is now certain, excluding possible, unexpected relativistic effects from consideration. Simple estimates show that further relativistic corrections on E_{pv} should remain small for this molecule. We note furthermore that the present calculations use a computational approach which is conceptually and practically quite different from the one we used previously. This provides independent confirmation of the increase in E_{pv} by an order of magnitude discovered in Ref. 21, compared to the earlier RHF-SDE results,[16] for the test case of hydrogen peroxide.

B. Ethylene

While CIS and RPA yield quite reasonable results for hydrogen peroxide, twisted ethylene is quite a different case. Here CIS and RPA must fail, since both methods require the validity of the RHF picture for the electronic ground state which is inadequate for twisted ethylene due to its biradicaloid character.[56] In singlet photochemistry ethylene is a well studied model system for photochemical *cis-trans*-isomerizations.[56,57] In triplet photochemistry it serves as a sample molecule for spin–orbit coupling effects in organic molecules and as a prototype for derivatives showing stereoselectivity in triplet photoreactions.[56] Consequently spin–orbit coupling in ethylene has been the subject of several semi-empirical and *ab initio* studies (see, e.g., Refs. 54, 58, and 59).

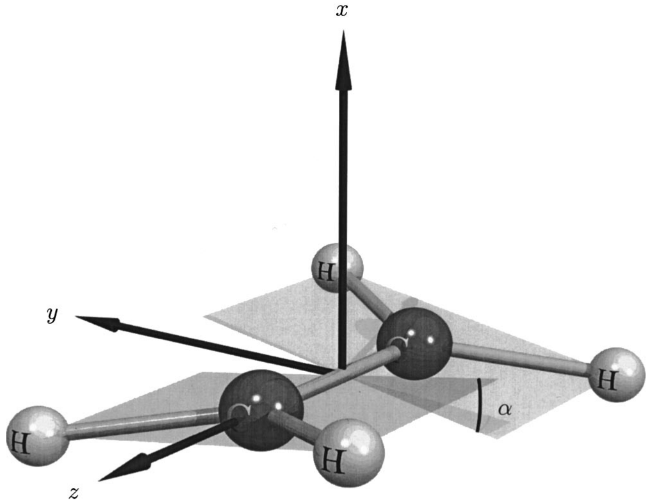

FIG. 5. Structure and orientation of the twisted ethylene enantiomer used in this study.

Also the parity violating potential has been calculated for slightly twisted ethylene,[14,15,22] since one might expect that the RHF picture of the electronic ground state still holds for those conformations. For larger twisting angles, however, the SDE-RHF as well as the CIS-RHF description is not physically justified, as has been shown numerically in Ref. 22.

Since the CASSCF method is suited to describe biradicals and biradicaloids we have applied the CASSCF-LR approach to the parity violating potential of twisted ethylene assuming the same geometry of the enantiomer used in previous studies,[15,16,22] that is C–C and C–H bond lengths of 132 pm and 107 pm, respectively and an H–C–C angle of 121.9° (see Fig. 5).

While planar ethylene exhibits the full D_{2h} symmetry, the twist motion lowers the symmetry to D_2 and reaches for a twist angle of 90° a configuration, which belongs to the point group D_{2d}. Since it has been shown in Ref. 22 that the total E_{pv} is the trace of a tensor with components $E_{\mathrm{pv}}^{ij}(i,j=x,y,z)$, we can now apply group theory to determine whether the components of E_{pv} must vanish for symmetry reasons. As the *i*th component of the spatial part of $\hat{H}_{\mathrm{pv}}$ transforms like the translation T_i and the *j*th component of the spatial part of $\hat{H}_{\mathrm{SO}}$ transforms as the rotation R_j, E_{pv}^{ij} is only nonvanishing, if the direct product of the irreducible representation (species) of T_i and the species of R_j contains the totally symmetric representation. We have compiled in analogy to Ref. 54 the ethylene-specific data in Table V where we have applied Mulliken's convention for the orientation of the molecule. Accordingly, E_{pv} must vanish for planar ethylene, since this conformation is achiral. Given this axis system, the E_{pv} tensor is diagonal for twisted ethylene.

TABLE V. Symmetry labels for ethylene.

α point group	0 D_{2h}	Variable D_2	90 D_{2d}
Γ for S_0	A_g	A	B_1
$\Gamma(R_x)$	B_{3g}	B_3	E
$\Gamma(R_y)$	B_{2g}	B_2	E
$\Gamma(R_z)$	B_{1g}	B_1	A_2
$\Gamma(T_x)$	B_{3u}	B_3	E
$\Gamma(T_y)$	B_{2u}	B_2	E
$\Gamma(T_z)$	B_{1u}	B_1	B_2
Vanishing Components E_{pv}^{ij} of E_{pv}	(all)	E_{pv}^{xy}, E_{pv}^{xz} E_{pv}^{yz}, E_{pv}^{yx} E_{pv}^{zx}, E_{pv}^{zy}	E_{pv}^{xz}, E_{pv}^{yz} E_{pv}^{zx}, E_{pv}^{zy} E_{pv}^{zz}

For 90°-twisted ethylene, however, the situation is a little more complicated, since the direct product $E\otimes E$ reduces to a direct sum $A_1\oplus A_2\oplus B_1\oplus B_2$, which contains the totally symmetric representation. Further inspection shows, that $T_xR_x+T_yR_y$ transforms as B_1 and $T_xR_x-T_yR_y$ as A_1. Therefore it follows that $E_{\mathrm{pv}}^{xx}=-E_{\mathrm{pv}}^{yy}$. Since $T_xR_y+T_yR_x$ transforms according to A_2 and $T_xR_y-T_yR_x$ according to B_2 both E_{pv}^{xy} and E_{pv}^{yx} must vanish.

In Table VI we report the results obtained with the CASSCF-LR method for a full-valence active space using various basis sets. In an exploratory study, where we applied an active space solely build from the π- and π^*-orbitals, we observed that for larger twisting angles the converged wave function was not stable in linear response calculations for triplet perturbation. That is, imaginary triplet excitation energies occurred. According to the requirements of Golab *et al.*[60] a proper approximation of the *N*th electronic state has to be variationally correct and the linear response calculation must be stable and yield $N-1$ negative excitation energies. Since the latter requirement was not met, we conclude that the wave function we obtained was not a proper representation of the S_0 state. Therefore, in the full-valence CASSCF calculation we verified explicitly the stability of each of the wave functions and computed the number of negative singlet and triplet excitation energies. For geometries in the vicinity of the D_{2d} conformation the wave functions computed using larger basis sets were unstable with respect to triplet perturbations. Although the values for the parity violating potentials for these structures are still reasonable, larger CASSCF expansions would be required in order to remove these instabilities.

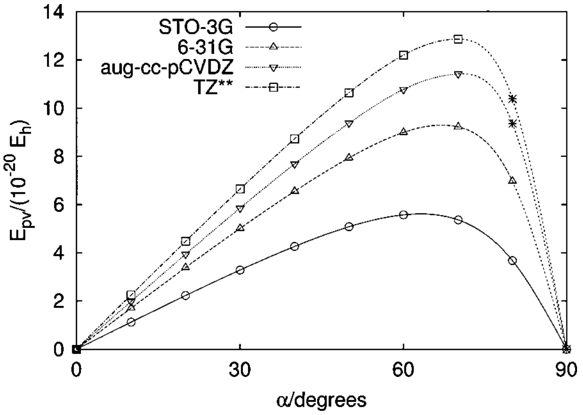

FIG. 6. Parity violating potential calculated with CASSCF-LR for various twisting angles of ethylene using various basis sets ($\sin^2\theta_w=0.25$). Data points marked with asterisks correspond to wave functions which are not stable with respect to triplet perturbations.

We display the parity violating potential in Fig. 6. The value for E_{pv} increases nearly linearly with increasing twisting angle, reaches a maximum at about 70° and then drops to vanishing E_{pv} for 90°-twisted ethylene, a behavior which cannot be reproduced with the CIS method and the RP approximation. The ethylene example emphasizes the importance of the MCLR approach for a more reliable calculation of parity violating effects in such molecules not well described by a single reference wavefunction. Figure 6 also demonstrates the relatively slow convergence of the calculated E_{pv} with basis set size.

IV. CONCLUSION

For current studies of the effects of parity violation in chiral molecules it is of great importance to provide a systematic approach to electroweak quantum chemistry, which not only supplies some practical quantum chemical working scheme, but also allows for an estimate of the reliability of the theoretical results and a route towards systematic improvements.

TABLE VI. Parity violating potential in ethylene calculated with CASSCF-LR for various twisting angles (results in parentheses are not based on a stable wave function).

Basis set	$E_{\mathrm{pv}}/(10^{-20}E_h)$ 10°	20°	30°	40°	50°	60°	70°	80°	90°
STO-3G	1.12	2.23	3.29	4.26	5.08	5.57	5.36	3.67	0.00
6-31G	1.71	3.39	5.01	6.55	7.93	8.99	9.22	6.97	(0.00)
6-31G[a]	1.58	3.14	4.65	6.08	7.36	8.34	8.55	6.46	(0.00)
aug-cc-pCVDZ	1.98	3.94	5.86	7.69	9.38	10.70	11.42	(9.36)	(0.00)
TZ**	2.25	4.48	6.65	8.72	10.63	12.20	12.86	(10.39)	(0.00)
TZ**[a]	2.09	4.15	6.16	8.09	9.86	11.31	11.92	(9.63)	(0.00)

[a] Experimental $\sin^2\theta_w$.

We have presented a multiconfiguration linear response approach to parity violating effects in molecules. This method allows the computation and the systematic study of E_{pv} at various levels of sophistication, beginning with the comparatively low-level approaches such as CIS and RPA progressing to CASSCF and finally approaching the full CI limit. This is especially valuable for the investigation of biologically relevant and spectroscopically accessible molecules, since we can judge with a few costly high-level benchmark calculations the performance and reliability of computationally less demanding approximations.

The calculations for hydrogen peroxide indicate that CIS and RPA give reasonable results for the parity violating potentials in this molecule. The random-phase approximation seems to be slightly superior when considering both the quality of the results and computational cost. The values obtained with the CASSCF-LR method are close to those of the much more expensive CISDT and CISDTQ(1sf) methods. The large variety of basis sets applied here to hydrogen peroxide suggests that diffuse functions are less important than tight functions. Nevertheless, a sufficient number of polarization functions is required, where ''sufficient'' depends on the method applied.

The investigation of twisted ethylene stresses the importance of a systematic approach to the calculation of parity violating effects. The MCLR method can be applied, where other methods must inherently fail such as for open shell systems, for excited electronic states and, as studied here, some unsaturated systems with partial open shell character. The methods developed here and demonstrated with the example ethylene can be applied to other unsaturated chiral systems such as allene derivatives and related molecules, which will be of interest to experimental approaches to measure E_{pv}.[24] The inherent accuracy of the approach renders it also suitable to calculate spectral properties such as frequency shifts in chiral molecules, which are of current interest.[26–28,61–64,66–69]

The MCLR approach is a well suited tool to provide theoretical information for on-going attempts to observe parity violating effects in molecules experimentally. As long as the parity violating Hamiltonian used in our calculation provides a reasonable picture of the underlying interactions we may assume that the computed values are close (at least as far as the order of magnitude is concerned) to the exact values. Relativistic effects are expected to be small for molecules involving only elements from the first rows of the periodic system as has been confirmed recently in relativistic calculations on H_2O_2 and H_2S_2[67] (and other molecules). However, future experiments have to provide the ultimate test for the validity of current theoretical approaches to the calculation of parity violating potentials.

ACKNOWLEDGMENTS

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