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Relativistic second-order many-body and density-functional theory for the parity-violation contribution to the C-F stretching mode in CHFClBr

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Relativistic four-component electronic structure theory using both wave-function (Dirac-Coulomb-Hartree-Fock and second-order many-body perturbation-theory) and density-functional based methods (local density, hybrid, and generalized gradient approximations) is applied to discuss the current status on the accuracy of parity-violation calculations for molecules. As a test case we choose the C-F stretching mode of CHFClBr, which is currently being investigated by molecular-beam spectroscopy. We show that electron correlation effects are important and cannot be neglected anymore for the parity nonconservation contribution to the total electronic energy. However, electron correlation contributions to parity violation in vibrational transitions of the C-F stretching mode are less important. The density functionals tested give somewhat different results, but the Becke three-parameter Lee-Yang-Parr functional agrees quite well with the second-order many-body perturbation-theory values. The calculations suggest that electron correlation effects have to be considered for future investigations in parity-violation effects in electronic transitions. The performance of density-functional based methods for this property needs further statistics.

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I. INTRODUCTION

The electroweak neutral current between electrons and nucleons causes a small difference in properties between the two enantiomers of a chiral molecule [1,2], which is roughly in the μHz–mHz region for vibrational, electronic, or NMR spectra [3,4]. It is therefore of no surprise that such effects have not yet been detected by experiment [3]. In the last few years great effort was made to search for suitable candidates with parity-violation (PV) effects in the 100-mHz–1-Hz region [5–7]. Perhaps the best chance to measure the breakdown of parity symmetry in molecules is by vibrational spectroscopy using a high-precision tuneable ultrastable CO_2 laser in a molecular-beam experiment [8]. In particular, the C-F stretching mode lies in the CO_2 frequency range and previous experiments therefore focused on the CHFClBr molecule [9,10].

It is clear that any successful observation of *P*-odd effects in molecules will require confirmation by theory. In atoms, relativistic many-body calculations for parity-violation amplitudes in forbidden electronic transitions include Breit and radiative corrections and agree with experiment to high accuracy, i.e., to 1% for the 6s-7s transition in Cs [11]. For molecules, such highly accurate relativistic many-body calculations including quantum electrodynamic effects are currently not feasible and a number of approximations are in use (see Ref. [12] for a comprehensive review). At the four-component relativistic level, parity-violation contributions are usually determined from Dirac-Coulomb Hartree-Fock (DC-HF) calculations neglecting electron correlation [13]. Electron correlation effects to the PV energy contribution are assumed to be rather small, as test calculations on H_2X_2 (X=O, S, Se, and Te) reveal [14,15]. Only in the case where the parity-violation contribution to the total energy comes close to zero, i.e., at torsion angles close to 90° in H_2X_2, electron correlation effects become important in a relative sense [14]. It was also noted that density-functional theory gives very similar results compared to Hartree-Fock for these systems [16].

To obtain an accurate value for the parity-violation contribution to the C-F stretching mode in CHFClBr or related molecules is a formidable task. Most applications have used a normal-mode analysis along the C-F stretching mode to determine the vibrational contributions to the parity-violation energy difference [17–19]. Such calculations show that anharmonicity effects have to be taken into account to get any reasonable value for the parity-violation contribution to the C-F stretching mode [17]. Even more interestingly, if vibrational coupling to other modes become important, as in the case of the deuterated species CDFClBr, such a one-dimensional treatment breaks down and strong enhancement effects to the parity violation are predicted for this molecule [7]. It also remains unclear how important electron correlation effects are in such molecules, and if relativistic density-functional theory is accurate enough to predict parity-violation contributions to molecular properties.

In two recent papers four-component density-functional and second-order many-body perturbation theory were outlined for the calculation of first-order molecular properties [15,20] with the four-component program package DIRAC [21]. Here we use both methods in the calculation of parity-violation energies in the C-F stretching mode of CHFClBr, to test the validity of these two different approaches to describe electron correlation.

II. COMPUTATIONAL DETAILS

Relativistic Hartree-Fock (HF), density-functional theory (DFT), and second-order many-body perturbation theory (MBPT2) calculations for CHFClBr were performed based on the Dirac-Coulomb Hamiltonian

$$H_{DC} = \sum_i \{c\vec{\alpha}_i \cdot \vec{p}_i + c^2\beta_i + V_{ext}(r_i)\} + \sum_{i<j} \frac{1}{r_{ij}} \qquad (1)$$

within the program package DIRAC [21]. $\vec{\alpha}$ and β are the well-known Dirac matrices in the standard representation. The external potential is the standard Coulombic potential accounting for the finite extension of the nucleus. An isotropic nuclear charge distribution for all elements was used [22]. $(SS|SS)$-type two-electron integrals were omitted in all calculations as such contributions can safely be neglected [13]. The basis sets for H, C, F, Cl, and Br were uncontracted *cc-pVDZ+np* sets [23,24] augmented by diffuse functions as detailed previously [13].

In the Dirac picture, the nuclear spin-independent P-odd operator responsible for the Z^0 exchange between electrons and nucleons, as derived from the timelike component of the vector nuclear-axial electron $(V_{\mathrm{n}}-A_{\mathrm{e}})$ coupling, for a given atom is [13]

$$H_{en}^{odd} = f\gamma_5,\; f = \frac{G_F}{2\sqrt{2}}[(1-4\sin^2\theta_w)Z - N]\rho(\vec{r}) = \frac{G_F}{2\sqrt{2}}Q_w\rho(\vec{r}), \qquad (2)$$

where G_F is the Fermi-coupling constant with a value of $G_F=(1.166\,37\pm0.000\,02)\times10^{-11}$ MeV^{-2} or $(2.222\,55\pm0.000\,04)\times10^{-14}$ a.u. The weak charge Q_W depends on the number of protons Z and neutrons N and the Weinberg mixing angle θ_w with $\sin^2\theta_w=0.2319$. $\rho(\vec{r})$ is the (normalized) weighted average over the proton and neutron distribution of the nucleus (approximated by a Gaussian distribution as mentioned above), and the Dirac matrix γ_5 is a 4×4 pseudoscalar chirality operator,

$$\gamma_5 = \gamma^5 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} = i\gamma^1\gamma^2\gamma^3\gamma^0, \qquad (3)$$

with I the 2×2 unit matrix and the 4×4 matrices γ^i are the Dirac matrices. For a multiparticle (many-atom) system the parity nonconserving energy shift E_{PV} at the Dirac-Coulomb Hartree-Fock (DC-HF) level is

$$E_{PV} = \sum_{\alpha}^{\text{nuclei}} E_{\mathrm{PV}}^{\alpha} = \langle\Psi_{HF}|H_{\mathrm{en}}^{\mathrm{odd}}|\Psi_{HF}\rangle$$
$$= \frac{G_F}{2\sqrt{2}} \sum_{\alpha}^{\text{nuclei}} Q_W^{\alpha} \sum_{I}^{\text{occupied spinors}} \langle\psi_I|\gamma^5\rho_\alpha(\vec{r}_\alpha)|\psi_I\rangle, \qquad (4)$$

where $\vec{r}_\alpha$ is the distance of an electron to nucleus α, and Ψ_{HF} is the Hartree-Fock wave function, composed of the four-component one-electron spinors ψ_I. Equation (4) shows that the parity-violation energy E_{PV} can be partitioned into individual atomic contributions E_{PV}^{α} convenient for further interpretations.

Four-component Kramers-restricted relativistic DFT is used within a Kohn-Sham formalism (for a detailed discussion see Refs. [20,25–27] to evaluate the matrix elements shown in Eq. (4). In Kohn-Sham theory the one-electron spinors ψ_I in Eq. (4) are replaced by the corresponding Kohn-Sham spinors, and the evaluation of the matrix elements in Eq. (4) becomes straightforward. It should be noted, though, that introduction of the PV interaction through Eq. (2) requires formally an extension of DFT because the appearance of the γ^5 prohibits the formulation of the energy solely in terms of the charge or current density. The functionals used were the local-density approximation (LDA) [28], the generalized gradient functionals of Becke, Lee, Yang, and Parr (BLYP) [29,30] and Perdew and Wang (PW86) [31], and the hybrid BLYP functional which contains HF exchange (B3LYP) [32] and is favored in most chemical applications. We use standard nonrelativistic functionals. Relativistic corrections to functionals appear to have negligible effect on calculated spectroscopic properties [33]; less is known about their effect on core properties. For more details see also Refs. [34,35].

The implementation of second-order many-body perturbation theory for the Dirac-Coulomb Hamiltonian allows for the calculation of analytical first-order molecular properties [15]. In contrast to variational approaches in which the first-order energy can be written as a simple expectation value over the optimized wave function, one needs to introduce a relaxed density matrix $D_{PQ}^{(2)}$ that contains the effect of electron correlation,

$$E_{PV}^{MBPT2} = E_{PV}^{HF} + E_{PV}^{(2)}\;; \quad E_{PV}^{(2)} = \sum_{P,Q} D_{PQ}^{(2)}\big(H_{en}^{odd}\big)_{QP}, \qquad (5)$$

where $(H_{en}^{odd})_{QP}$ is the property matrix for the electroweak perturbation in the molecular spinor basis. Explicit expressions for $D_{PQ}^{(2)}$ are given in Ref. [15] and are based on the canonical expression for the MBPT2 correlation energy [36],

$$E^{(2)} = \frac{1}{4} \sum_{I,J}^{\text{occupied spinors}} \sum_{A,B}^{\text{virtual spinors}} \tau_{IJ}^{AB}\langle AB\,\|\,IJ\rangle \text{ and}$$
$$\tau_{IJ}^{AB} = \frac{\langle IJ\,\|\,AB\rangle}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B}. \qquad (6)$$

The summation over virtual spinors (A, B) is restricted to positive energy solutions only, but negative energy solutions enter in the calculation of the full response of the wave function to the perturbing operator. In the definition of the MBPT2 energy one may furthermore choose to neglect excitations from the lowest occupied spinors and delete high energy virtual spinors to obtain a more economical scheme. In the present work we applied an energy threshold of 100 a.u. for inclusion of virtual spinors and kept the bromine 1*s*, 2*s*, and 2*p* and the chlorine 1*s* spinor frozen. This is consistent with the active space chosen in earlier work on H_2S_2 and H_2Se_2 [15]. Since the operator given in Eq. (4) is given as a sum over atoms it is possible to also split the correlation

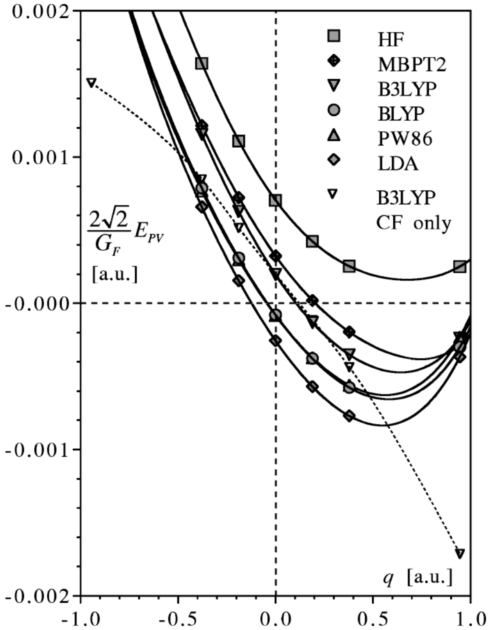

FIG. 1. Electroweak contribution $E_{\mathrm{PV}}(q)$ to the total electronic energy (scaled by $2\sqrt{2}/G_F$) as a function of the C-F stretching along the normal-mode coordinate q at various levels of theory (in a.u.). $q=0$ defines the equilibrium C-F bond distance. For the B3LYP CF only calculation, see text.

contribution into terms relating to the individual atoms in the molecule.

A normal-mode analysis gave the harmonic force field F_{xy} and corresponding displacement coordinates for the C-F stretching mode from scalar relativistic coupled cluster calculations [CCSD(T), i.e., singles-doubles coupled cluster with triples treated perturbatively], which as expected is the most intense IR mode in the CO_2 laser frequency range. Along the C-F displacement q of the normal mode the CCSD(T) potential-energy curve $V(q)$ was calculated stepwise and fitted to a polynomial in q of sufficiently high order,

$$V(q) = V(0) + \sum_{k=2} \frac{1}{k!} V^{[k]}(0) q^k. \tag{7}$$

The detailed procedure together with the fit parameters for the coupled cluster potential curve can be found in Ref. [37]. The parity-violating contributions to the total electronic energy per atom, $E_{PV}^{\alpha}(q)$, were calculated pointwise along the CCSD(T) potential-energy curve $V(q)$ for the R configuration of CHFClBr and fitted to a polynomial of order 6,

$$E_{PV}(q) = \sum_{\alpha} E_{PV}^{\alpha}(q) = E_{PV}(0) + \sum_{k=1}^{6} \frac{1}{k!} E_{PV}^{[k]}(0) q^k, \tag{8}$$

as shown in Fig. 1 [note the different meaning of $E_{PV}^{[2]}$ here and $E_{PV}^{(2)}$ in Eq. (5)]. The polynomial fitting procedure does affect slightly the vibrational contributions and care must be taken that the Taylor expansion is sufficiently accurate along the equilibrium geometry. $q=0$ defines the minimum geometry, and $q>0$ implies C-F bond distances great than the minimum distance. A Numerov-Cooley [38] procedure for solving the vibrational Schrödinger equation numerically over a grid of 5000 points gave the parity-violation energy shifts for each vibrational level with quantum number n in first-order perturbation theory,

$$E_{PV,n} = \langle n | E_{PV}(q) | n \rangle, \tag{9}$$

where $E_{PV,n}$ is the parity-violation energy contribution to a vibrational level with quantum number n. A reduced mass of $\mu=9.703$ amu was used for the C-F stretching mode obtained from a coupled cluster normal-mode treatment [37]. For CHFClBr there are no other modes close to the C-F stretching frequency within 100 cm^{-1} (in contrast to CDFClBr) and higher-order coupling with other modes for the fundamental transition is neglected in this study. Nevertheless, the overtones reported here have to be taken with care.

III. RESULTS

Table I shows the calculated electroweak energy contribution E_{PV} to the total electronic energy at $q=0$, which is also shown in Fig. 1 as a function of displacements q along the C-F stretching normal mode. It came to quite a surprise that the difference between the HF, DFT, and MBPT2 are so large in relative terms. The value obtained from the LDA approximation even has the opposite sign compared to the MBPT2 value. If we accept that the MBPT2 result represents the most accurate value, then perhaps the B3LYP functional performs best. However, such a conclusion has to be taken with

TABLE I. Parity-violation contribution E_{PV} to the total electronic energy at the equilibrium geometry of CHFClBr ($q=0$). All values are in a.u. The values for $E_{PV}^{[1]}(0)$ and $E_{PV}^{[2]}(0)$ have been derived from a sixth-order polynomial fit. The square brackets denote powers of 10.

Property	Atom	HF	MBPT2	B3LYP	BLYP	PW86	LDA
E_{PV}^{α}	H	2.811[−24]	6.272[−24]	1.167[−23]	1.433[−23]	1.467[−23]	1.614[−23]
	C	5.752[−20]	7.104[−20]	6.890[−20]	6.837[−20]	7.131[−20]	7.736[−20]
	F	8.798[−19]	9.158[−19]	1.030[−18]	1.023[−18]	1.002[−18]	1.048[−18]
	Cl	−3.598[−18]	−2.895[−18]	−2.835[−18]	−2.170[−18]	−2.009[−18]	−1.702[−18]
	Br	8.192[−18]	4.444[−18]	3.280[−18]	4.506[−19]	2.792[−19]	−1.433[−18]
$E_{PV}=\Sigma_{\alpha}E_{PV}^{\alpha}$		5.530[−18]	2.536[−18]	1.544[−18]	−6.279[−19]	−6.569[−19]	−2.009[−18]
$E_{PV}^{[1]}(0)= \partial E_{PV}/\partial q\|_{q=0}$		−1.424[−17]	−1.463[−17]	−1.581[−17]	−1.433[−17]	−1.400[−17]	−1.513[−17]
$E_{PV}^{[2]}(0)= \partial^2 E_{PV}/\partial q^2\|_{q=0}$		2.806[−17]	2.138[−17]	2.308[−17]	1.984[−17]	1.996[−17]	2.124[−17]

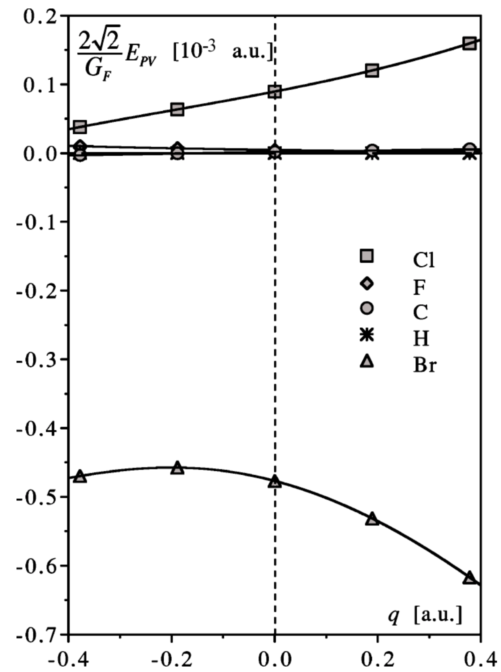

FIG. 2. Electroweak electron correlation contribution $E_{PV}^{\alpha}(q)$ per atom obtained from MBPT2 calculations as a function of the C-F stretching along the normal mode (scaled by $2\sqrt{2}/G_F$ and in 10^{-3} a.u.). $q=0$ defines the equilibrium C-F bond distance.

care since more statistics are needed to reliably assess the performance of DFT for core properties. Earlier work on electric-field gradients shows that errors in the DFT approach are not systematic [39–41], and there is not a preferable choice of density functional available for such a property.

Figure 1 shows that all the parity violation curves go through a minimum and start to increase again at larger C-F bond distances. We mention that the dissociation limit (CHClBr+F) would lead to a nonzero parity-violation contribution due to the fact that the fragment CHClBr would be nonplanar. It is therefore no surprise that the largest contribution still comes from the bromine atom at these distances.

Electron correlation more than halves the original HF E_{PV} value, Table I. Hence, in contrast to all previous assumptions [5,12,14,15], electron correlation effects are important, and the conclusions drawn previously on the basis of calculations on simple systems such as H_2O_2 or H_2S_2 have to be revised. We mention that for these four-atomic molecules even nonrelativistic DFT gives reliable results [16]. In order to analyze this rather large effect in more detail, we partition the electroweak energy into contributions arising from different atoms. The individual contributions for each atom at $q=0$ are also listed in Table I.

It is evident that the most important contributions are coming from the two heavy elements, chlorine and bromine, and they cancel each other out to some extent except for the LDA approximation where they have the same sign. The same is true for the electron correlation contribution to E_{PV} at the MBPT2 level of theory as shown in Fig. 2 (only shown for a limited distance range since the closed-shell methods used in this work will diverge at large C-F bond distances). Figure 3 finally shows the individual orbital contributions to the parity-violation matrix element for the two methods, HF and LDA. Even if one should not strictly compare HF with Kohn-Sham orbitals, we clearly see that the major contributions come from the valence region, i.e., the highest occupied nine valence orbitals consisting mostly of the C, F, Cl, and Br *p* orbitals and the H *1s* (the 19 core orbitals are not included in this graph since they only contribute little to the total parity-violation energy). Large differences between both methods appear for the valence orbitals 31 and 32 which mostly consist of bromine and chlorine *p* orbitals.

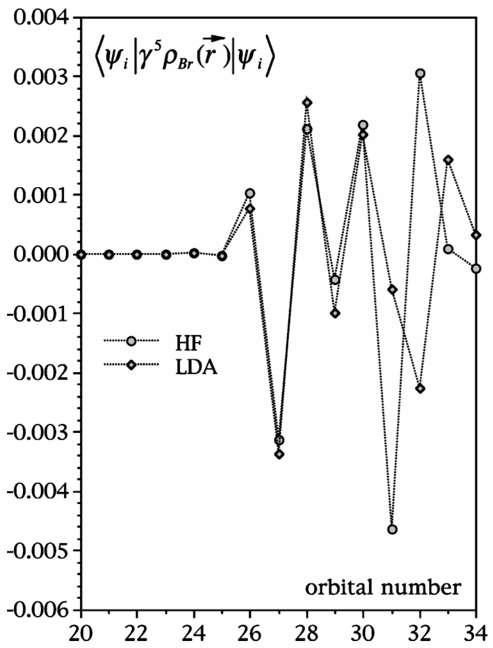

FIG. 3. Individual orbital contributions to the parity-violation energy contribution for the bromine atom at the HF and LDA level of theory. Orbital 34 defines the highest occupied molecular orbital.

The question now is how such large differences in E_{PV} between the different methods applied will influence the parity-violation contribution to vibrational transitions, since this relates to a measurable quantity. From perturbation theory using Eqs. (7) and (8) the parity-violation energy shifts for each vibrational level *n* is approximately given by

$$E_{PV,n} = E_{PV}(0) + \frac{1}{2}\left(\frac{\hbar}{\mu\omega_e}\right)\left[E_{PV}^{[2]}(0) - \left(\frac{1}{\mu\omega_e^2}\right)V^{[3]}(0)E_{PV}^{[1]}(0)\right] \times\left(n+\frac{1}{2}\right) + \cdots, \qquad (10)$$

where μ, ω_e, and $V^{[3]}(0)$ are the reduced mass, harmonic vibrational frequency, and cubic force constant of the C-F stretching normal mode. $E_{PV}(0)$ is the parity-violation energy at equilibrium geometry $q=0$, and the derivatives are taken with respect to the displacement coordinate q as detailed in Eq. (8). The formula corresponds to the formula given for vibrationally corrected properties of diatomic molecules by Schlier [42] and Buckingham [43,44]. For higher-order contributions, see Ref. [45]. We did not use formula (10) but rather chose a numerical solution of the vibrational Schrödinger equation, because such a treatment automati-

TABLE II. Parity-violation contribution $E_{PV,n}$ to the C-F vibrational mode from a normal-mode analysis of CHFClBr. All values are in 10^{-18} a.u. For the B3LYP CF only calculation, see text.

Method	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=0\rightarrow 1$	$n=0\rightarrow 2$
HF	5.458	5.319	5.190	5.069	4.957	−0.1385	−0.1295
MBPT2	2.441	2.255	2.077	1.906	1.741	−0.1855	−0.1781
B3LYP	1.442	1.244	1.057	0.881	0.717	−0.1979	−0.1870
B3LYP CF only	1.412	1.143	0.866	0.581	0.286	−0.2688	−0.2767
BLYP	−0.724	−0.908	−1.081	−1.241	−1.388	−0.1843	−0.1727
PW86	−0.748	−0.925	−1.089	−1.240	−1.377	−0.1760	−0.1640
LDA	−2.109	−2.301	−2.479	−2.642	−2.789	−0.1915	−0.1777

cally includes higher-order anharmonicity effects. Nevertheless, formula (10) is interesting since it shows that the most important vibrational contribution to a molecular property comes from either the curvature of the property [in our case $E_{PV}^{[2]}(0)$] or from the anharmonicity of the potential-energy curve [through the cubic force constant and $V^{[3]}(0)$] combined with the slope of the property curve [$E_{PV}^{[1]}(0)$]. It is obvious that a linear behavior in $E_{PV}(q)$ together with a harmonic potential-energy curve [$V^{[3]}(0)=0$] leads to $E_{PV,n}=\text{const}$ for all vibrational levels n. Hence for parity-violation effects in vibrational transitions the pure electronic contribution E_{PV}^{α} at $q=0$ is of little interest. We therefore include the data for the first and second derivatives of the parity-violation energy contribution with respect to the C-F stretching mode, i.e., $E_{PV}^{[1]}(0)$ and $E_{PV}^{[2]}(0)$, in Table I as well.

Interestingly, the variation between the different methods for both $E_{PV}^{[1]}(0)$ and $E_{PV}^{[2]}(0)$ are not great, i.e., we obtain $E_{PV}^{[1]}(0)=-(1.5\pm 0.1)\times 10^{-17}$ a.u. and $E_{PV}^{[2]}(0)=+(2.4\pm 0.4)\times 10^{-17}$ a.u. Hence we expect much less variation in the predicted vibrational parity-violation effects. Moreover, since the cubic force constant is negative, the second term in Eq. (10) coming from (negative) $E_{PV}^{[1]}(0)$ will result in a lower $E_{PV,n}$ while the positive curvature $E_{PV}^{[2]}(0)$ will result in a positive contribution to $E_{PV,n}$. It turns out that for the vibrational ground state the major contribution comes from the $E_{PV}^{[1]}(0)$ term of Eq. (10) with -0.16×10^{-18} a.u., and only $+0.06\times 10^{-18}$ a.u. from the first term dependent on $E_{PV}^{[2]}(0)$. Hence the result will critically depend on the accuracy of the cubic force constant. As expected, for both $E_{PV}^{[1]}(0)$ and $E_{PV}^{[2]}(0)$ the major contributions come from the Cl and Br atoms.

A detailed vibrational analysis is shown in Table II. The contributions to each vibrational level differ significantly due to the constant term E_{PV} that varies widely with the method that is employed. This term, however, cancels out for the vibrational transitions where we observe only small changes between the different methods (this term, however, does *not* cancel out in electronic transitions). For the fundamental transition the parity-violation effect varies only from -1.39×10^{-19} a.u. for HF to -1.98×10^{-19} a.u. for B3LYP. If we take the most reliable MBPT2 value we predict a change of -1.86×10^{-19} a.u. which is equal to −1.2 mHz. Hence for the difference between both enantiomers we obtain $\Delta\upsilon_{\rm RS}=\upsilon_{\rm R}-\upsilon_{\rm S}=-2.4$ mHz. This is an enhancement of 34% compared to the previous best HF value [37]. Hence for the ratio $\Delta\upsilon_{\rm RS}/\upsilon_{\rm CF}$ we obtain -7.56×10^{-17} with $\upsilon_{\rm CF}=1077\ \text{cm}^{-1}$ for the C-F stretching mode [46]. This value also compares well with the recent result of Quack and Stohner obtained in the Schrödinger picture using linear-response theory, i.e., $\Delta\upsilon_{\rm RS}/\upsilon_{\rm CF}=-8.06\times 10^{-17}$ [7]. This might be surprising since a major contribution to the parity violation comes from the heavy atom ligand bromine. However, the inner core orbitals for which relativistic effects are most important contribute only little to the total parity-violation shift. Another source for this difference lies in the different treatment for electron correlation and the vibrational analysis.

Another important question not addressed before is where the major contribution to the parity-violation frequency shift is coming from. The C-F normal mode nicely correlates in a linear fashion with the pure C-F stretch [37] and one might naively expect that the major contribution comes from the change in the C-F bond distance only. We tested this assumption by performing additional calculations at the B3LYP level of theory in which we fixed the coordinates of all atoms in the CHClBr fragment to their equilibrium value and varied only the C-F internal coordinate. This pure C-F stretching contribution is also shown in Fig. 1. While the first derivative $E_{PV}^{[1]}(0)=-1.295\times 10^{-17}$ a.u. does indeed not change significantly, the second derivative is decreasing by one order of magnitude, $E_{PV}^{[2]}(0)=+2.468\times 10^{-18}$ a.u. Larger changes are clearly observed in regions further away from the equilibrium geometry, indicating that the influence of the movement of the other atoms lead to a change in the wave function that cannot be neglected. Table II shows that the parity-violation contribution to the ground state changes little, but as mentioned before, this contains the largest term, the parity-violation energy change for the equilibrium structure. Since the second derivative is now greatly diminished, the parity-violation contribution to the fundamental transition is overestimated by as much as 36%. In fact, the next hot band now shows an increase in the parity-violation contribution in contrast to the more exact B3LYP values where the true normal coordinate is followed. Hence the quadratic coupling term caused by the off-diagonal force constants (in terms of internal coordinates) cannot be neglected.

Finally, for obtaining more accurate vibrational parity-violation contributions also the contribution from other modes may have to be considered. Since analytical deriva-

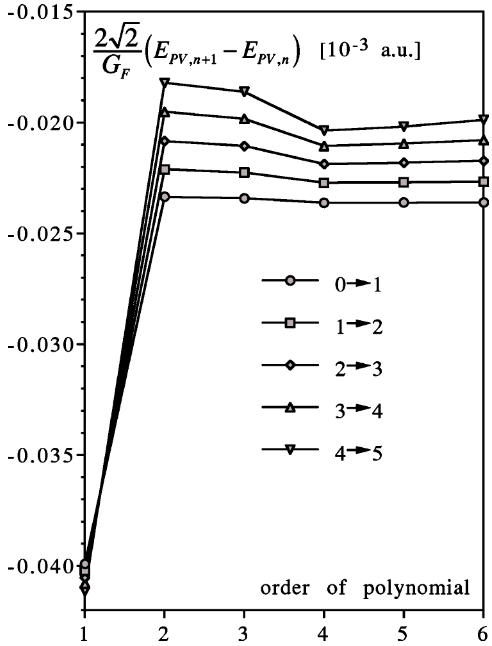

FIG. 4. Convergence of the parity-violation contribution to the $n \rightarrow (n+1)$ vibrational transition for the fundamental ($n=0$) and several hot bands ($n>0$) (scaled by $2\sqrt{2}/G_F$). From MBPT2 calculations.

tives of the parity-violation energy with respect to nuclear displacements are not yet implemented into the four-component formalism, a numerical treatment requires a large number of calculations along the nine-dimensional potential-energy surface. Therefore Quack and Stohner restricted their analysis to a four-dimensional subspace including the vibrations which strongly couple to the C-F stretching mode in CDFClBr [7]. They also used a Taylor expansion up to third order for the parity violation along the normal coordinates. For future investigations it is therefore important to know how relevant higher-order terms are in this expansion. Figure 4 shows the convergence of the parity-violation contribution to the fundamental transition and several hot bands with increasing order of the polynomial used in the vibrational analysis. The message is clear. For the fundamental transition and the first hot band a second degree polynomial is sufficient. Only for the upper vibrational levels a polynomial of a higher degree than 2 is perhaps needed. This is good news for future investigations since for a fully coupled nine-dimensional vibrational analysis only a Taylor expansion up to second order of the parity-violation energy contribution with respect to the normal coordinates is required.

IV. CONCLUSIONS

For the parity-violation contribution to the total energy E_{PV}, electron correlation cannot be neglected anymore and more sophisticated electron correlation procedures are needed in future to predict precise parity-violation effects in molecules. Density-functional methods have to be carefully tested against more accurate *ab initio* methods, possibly for a larger number of molecules, in order to decide if DFT will be useful for such calculations. For vibrational transitions $n \rightarrow n'$ the total contribution E_{PV} cancels out, and only the gradient $\partial E_{PV}/\ \partial q_i|_{\vec{q}=0}$ and second derivative matrix $\partial^2 E_{PV}/\ \partial q_i \partial q_j|_{\vec{q}=0}$ of the parity-violation energy with respect to the coordinates $\vec{q}$ along the normal mode becomes important. Interestingly, they do not vary much between different approximations and previous predictions made are therefore still valid.

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