Theor Chem Acc (2000) 103:365–373
DOI 10.1007/s002149900078

Theoretical
Chemistry Accounts

Regular article

A modified variation–perturbation approach to zero-point vibrational motion

Per-Olof Åstrand[1], **Kenneth Ruud**[2,*], **Dage Sundholm**[3]

[1] Condensed Matter Physics and Chemistry Department, Risø National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark
[2] Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway
[3] Department of Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 Helsinki, Finland

Received: 16 April 1999 / Accepted: 1 July 1999 / Published online: 4 October 1999

Abstract. We present a detailed investigation of the perturbation approach for calculating zero-point vibrational contributions to molecular properties. It is demonstrated that if the sum of the potential energy and the zero-point vibrational energy is regarded as an effective potential energy, the leading contribution to the first-order wave function vanishes in the perturbation approach. Two different perturbation approaches have been investigated numerically by calculations of some magnetic properties for a few diatomic molecules and the results obtained have been compared to the exact numerical results. It is shown that only a few terms need to be included in a perturbation expansion to obtain an accuracy in the calculated rovibrational contribution better than the quality normally obtained for the potential and property surfaces in electronic structure calculations.

Key words: Zero-point vibrations – Variation-perturbation method

1 Introduction

The vibrational part of the molecular wave function may be calculated to high accuracy for diatomic, triatomic and sometimes even slightly larger molecules [1–10]. For polyatomic molecules, molecular complexes and condensed phases, however, it is much more difficult to go beyond the harmonic approximation. A few years ago, a method where the zero-point vibrational energy was treated as an additional potential energy was introduced and applied to the calculation of intermolecular vibrational frequencies of bimolecular complexes [11]. The method has also been applied to calculate rovibrational averages of magnetic properties of diatomic molecules [12–15] and results close to those obtained using numerical integration have been obtained [12]. In the approach, the zero-point vibrational average of a molecular property Ω for a diatomic molecule is given as [12]

$$\langle\Omega\rangle = \Omega_{\text{eff}} + \frac{\Omega^{(2)}_{\text{eff}}}{4m\omega_{\text{eff}}} \quad , \tag{1}$$

where eff denotes that the property has been calculated at an effective geometry, which is the minimum of the surface defined by the sum of the potential energy and the zero-point vibrational energy. In Eq. (1), m is the reduced mass, ω the harmonic frequency, and $\Omega^{(2)}$ the second derivative of the molecular property with respect to the bond distance. The approach corresponds to a harmonic oscillator approximation, expanded around a variationally determined expansion point, and thus has clear connections to variational transition-state theory [16] and to an approach by Bishop and Pipin [17]. However, no investigation of the importance of higher-order terms in the expansion of the potential and property surfaces has been carried out for this approach.

The purpose of this work is to analyze higher-order contributions to Eq. (1) in terms of the variation–perturbation approach by Kern and Matcha [18], which in turn is based on the approach used by Hylleraas [19] in 1930 for calculating the energy of the He atom. We demonstrate that by expanding around an effective geometry instead of the equilibrium geometry, the most important higher-order term vanishes. We present results for different magnetic properties of four diatomic molecules, and compare these to the results obtained using numerical integration.

2 Theory

The purpose of this section is to analyze the approach introduced in Ref. [11] for calculating vibrationally averaged molecular properties [12] in terms of the variation–perturbation approach [18]. We will restrict ourselves to the vibrational ground state and to diatomic molecules, but extensions to vibrationally excited

---

[*] *Present address*: San Diego Supercomputer Center, University of California at San Diego, 9500 Gilman Drive Dept. 0505, La Jolla, CA 92093-0505, USA

Correspondence to: P.-O. Åstrand

states [20] and polyatomic molecules [18] are straightforward.

The potential energy may be expanded around an arbitrary expansion point r_{exp} as

$$V(q) = V^{(0)}_{\mathrm{exp}} + V^{(1)}_{\mathrm{exp}} q + \frac{1}{2} V^{(2)}_{\mathrm{exp}} q^2 + \frac{1}{6} V^{(3)}_{\mathrm{exp}} q^3 + \frac{1}{24} V^{(4)}_{\mathrm{exp}} q^4 + \cdots \ , \tag{2}$$

where $q = r - r_{\mathrm{exp}}$ is the deviation from the expansion point and $V^{(n)}_{\mathrm{exp}}$ is the nth derivative of the potential with respect to q calculated at r_{exp}. If the quadratic term is included in the zeroth-order Hamiltonian and the remaining terms are treated as perturbations, we have

$$H^{(0)} = \frac{p^2}{2m} + \frac{1}{2} V^{(2)}_{\mathrm{exp}} q^2 \ , \tag{3}$$

where the first term on the right-hand side is the ordinary kinetic-energy operator. This is the Hamiltonian for a harmonic oscillator, which has the well-known eigenvalues

$$E^{(0)}_n = (n + \tfrac{1}{2})\omega \ , \tag{4}$$

and eigenfunctions

$$\Psi^{(0)}_n = N_n H_n(\xi) \mathrm{e}^{-\frac{1}{2}\xi^2} \ , \tag{5}$$

where $\omega = \sqrt{(V^{(2)}/m)}$, $\xi = \sqrt{m\omega} q$, n is the vibrational quantum number, N_n are normalization constants and $H_n(\xi)$ are Hermite polynomials. Normally, the expansion of the potential in Eq. (2) is carried out around the equilibrium geometry r_{e} where $V^{(1)}_{\mathrm{e}} = 0$. In our approach [11, 12], however, another expansion point is adopted. By choosing the Hamiltonian as

$$H = H^{(0)} + V^{(0)}_{\mathrm{exp}} \ , \tag{6}$$

and the Harmonic oscillator wave function $\Psi^{(0)}_0$ in Eq. (5) as a trial function and minimizing the energy functional

$$\tilde{E}^{(0)} = V^{(0)}_{\mathrm{exp}} + \langle \tilde{\Psi}^{(0)}_0 | H^{(0)} | \tilde{\Psi}^{(0)}_0 \rangle = V^{(0)}_{\mathrm{exp}} + \frac{1}{2}\omega_{\mathrm{exp}} \ , \tag{7}$$

with respect to the expansion point, r_{exp}, an optimized expansion point, r_{eff}, is found. Thus, both the optimized expansion point, r_{eff}, and the corresponding harmonic frequency, ω_{eff}, have been determined in the variational procedure. The second term on the right-hand side of Eq. (7) is the zero-point vibrational energy, and we thus see that carrying out the Taylor expansion of the potential around r_{eff} instead of around the equilibrium geometry, r_{e}, is an improvement compared to the conventional harmonic oscillator approximation [11]. In variational transition-state theory [16], the zero-point vibrational energies of all modes other than that describing the reaction path are included in the Hamiltonian used in the variational procedure; thus, this part of the zero-point vibrational energy can be regarded as an additional potential energy. In our approach, however, we include the total zero-point vibrational energy in the variational treatment [11]. Furthermore, we note that when $\tilde{E}^{(0)}$ in Eq. (7) is minimized with respect to the expansion point, the condition

$$V^{(1)}_{\mathrm{eff}} + \frac{V^{(3)}_{\mathrm{eff}}}{4m\omega_{\mathrm{eff}}} = 0 \ , \tag{8}$$

is fulfilled. If we regard the remaining terms in the expansion of the potential in Eq. (2) as perturbations

$$H^{(1)} = V^{(1)}_{\mathrm{exp}} q + \frac{1}{6} V^{(3)}_{\mathrm{exp}} q^3 \ , \tag{9}$$

and

$$H^{(2)} = \frac{1}{24} V^{(4)}_{\mathrm{exp}} q^4 \ , \tag{10}$$

and apply Rayleigh–Schrödinger perturbation theory [21]

$$\begin{aligned} \langle \Psi | H - E | \Psi \rangle = \langle \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots | \\ \times (H^{(0)} - E^{(0)}) + \lambda (H^{(1)} - E^{(1)}) \\ + \lambda^2 (H^{(2)} - E^{(2)}) + \cdots | \Psi^{(0)} + \lambda \Psi^{(1)} \\ + \lambda^2 \Psi^{(2)} + \cdots \rangle \ , \end{aligned} \tag{11}$$

where λ is an order parameter and the subscript n in Eqs. (4) and (5) has been dropped since only the vibrational ground state ($n = 0$) is considered. By solving Eq. (11) for each order of λ, the first-order correction to the energy is found to be

$$E^{(1)} = \langle \Psi^{(0)} | H^{(1)} | \Psi^{(0)} \rangle \ , \tag{12}$$

which vanishes since $H^{(1)}$ in Eq. (9) is odd with respect to the geometrical displacement q. The second-order energy, $E^{(2)}$, can be regarded as an energy functional [18],

$$\tilde{E}^{(2)} = \langle \Psi^{(0)} | H^{(2)} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | H^{(1)} | \tilde{\Psi}^{(1)} \rangle + \langle \tilde{\Psi}^{(1)} | H^{(0)} - E^{(0)} | \tilde{\Psi}^{(1)} \rangle \ , \tag{13}$$

which can be minimized with respect to the trial function $\tilde{\Psi}^{(1)}$. We expand the first-order wave function in a complete set of harmonic oscillator wave functions (see Eq. 5)

$$\tilde{\Psi}^{(1)} = \sum_{r=1}^{\infty} a^{(1)}_r \Psi^{(0)}_r \ , \tag{14}$$

where $\Psi^{(0)}_0$ is the wave function obtained in Eq. (7). We thus get

$$\frac{\partial \tilde{E}^{(2)}}{\partial a^{(1)}_r} = 2V^{(1)} \langle q \rangle_{0r} + \frac{1}{3} V^{(3)}_{\mathrm{exp}} \langle q^3 \rangle_{0r} + 2 a^{(1)}_r \langle H^{(0)} - E^{(0)} \rangle_{rr} \ , \tag{15}$$

where we have used the notation $\langle H \rangle_{ps} = \langle \Psi^{(0)}_p | H | \Psi^{(0)}_s \rangle$. These integrals can be evaluated by standard procedures, and we find

$$a^{(1)}_r = \frac{-\left(2V^{(1)}_{\mathrm{exp}} \langle q \rangle_{0r} + \frac{1}{3} V^{(3)}_{\mathrm{exp}} \langle q^3 \rangle_{0r} \right)}{2 \langle H^{(0)} - E^{(0)} \rangle_{rr}} \ . \tag{16}$$

Note that the only two non-zero terms are $a^{(1)}_1$ and $a^{(1)}_3$. Following the approach by Kern and Matcha [18], the potential is expanded around r_{e} and the coefficients become

$$a_1^{(1)} = \frac{-V_{\mathrm{e}}^{(3)}}{4\sqrt{2}\omega_{\mathrm{e}}(m\omega_{\mathrm{e}})^{\frac{3}{2}}} \tag{17}$$

and

$$a_3^{(1)} = \frac{-V_{\mathrm{e}}^{(3)}}{12\sqrt{3}\omega_{\mathrm{e}}(m\omega_{\mathrm{e}})^{\frac{3}{2}}} \ , \tag{18}$$

where the subscript e denotes that the properties are calculated at the equilibrium geometry.[1] In comparison with the work by Kern and Matcha [18], the only extension here is that we expand the potential around r_{eff} instead of around r_{e}. It can then be shown that $a_1^{(1)}$becomes zero because of the condition in Eq. (8), whereas $a_3^{(1)}$ is similar to Eq. (18)

$$a_3^{(1)} = \frac{-V_{\mathrm{eff}}^{(3)}}{12\sqrt{3}\omega_{\mathrm{eff}}(m\omega_{\mathrm{eff}})^{\frac{3}{2}}} \ , \tag{19}$$

since $\langle q \rangle_{03} = 0$. We thus see that the leading higher-order term of the wave function vanishes if the expansion point is determined variationally. If the same procedure is carried out for the second-order wave function, we obtain

$$a_s^{(2)} = -\frac{\frac{1}{12} V_{\mathrm{exp}}^{(4)} \langle q^4 \rangle_{0s} - \sum_{r=1,3} \left(2V_{\mathrm{exp}}^{(1)} \langle q \rangle_{rs} + \frac{1}{3} V_{\mathrm{exp}}^{(3)} \langle q^3 \rangle_{rs} \right) a_r^{(1)}}{2\langle H^{(0)} - E^{(0)} \rangle_{ss}} \ , \tag{20}$$

where $a_s^{(2)} \neq 0$ for $s = 2, 4, 6$. For an expansion around the equilibrium geometry (where $V_{\mathrm{e}}^{(1)} = 0$) we obtain

$$a_2^{(2)} = \sqrt{2} \left(\frac{-V_{\mathrm{e}}^{(4)}}{32\omega_{\mathrm{e}}(m\omega_{\mathrm{e}})^2} + \frac{3V_{\mathrm{e}}^{(3)^2}}{64\omega_{\mathrm{e}}^2(m\omega_{\mathrm{e}})^3} \right) \ , \tag{21}$$

$$a_4^{(2)} = \sqrt{\frac{3}{2}} \left(\frac{-V_{\mathrm{e}}^{(4)}}{96\omega_{\mathrm{e}}(m\omega_{\mathrm{e}})^2} + \frac{7V_{\mathrm{e}}^{(3)^2}}{288\omega_{\mathrm{e}}^2(m\omega_{\mathrm{e}})^3} \right) \ , \tag{22}$$

and

$$a_6^{(2)} = \frac{\sqrt{5}V_{\mathrm{e}}^{(3)^2}}{432\omega_{\mathrm{e}}^2(m\omega_{\mathrm{e}})^3} \ , \tag{23}$$

which is consistent with the results of Sprandel and Kern [22]. If we instead carry out the expansion around the effective geometry (where $a_1^{(1)} = 0$), we obtain

$$a_2^{(2)} = \sqrt{2} \left(\frac{-V_{\mathrm{eff}}^{(4)}}{32\omega_{\mathrm{eff}}(m\omega_{\mathrm{eff}})^2} + \frac{V_{\mathrm{eff}}^{(3)^2}}{96\omega_{\mathrm{eff}}^2(m\omega_{\mathrm{eff}})^3} \right) \ , \tag{24}$$

$$a_4^{(2)} = \sqrt{\frac{3}{2}} \frac{1}{96} \left(\frac{-V_{\mathrm{eff}}^{(4)}}{\omega_{\mathrm{eff}}(m\omega_{\mathrm{eff}})^2} + \frac{V_{\mathrm{eff}}^{(3)^2}}{\omega_{\mathrm{eff}}^2(m\omega_{\mathrm{eff}})^3} \right) \ , \tag{25}$$

and

$$a_6^{(2)} = \frac{\sqrt{5}V_{\mathrm{eff}}^{(3)^2}}{432\omega_{\mathrm{eff}}^2(m\omega_{\mathrm{eff}})^3} \ . \tag{26}$$

Compared to the expansion around the equilibrium geometry, the $V_{\mathrm{exp}}^{(4)}$ terms are equivalent, whereas the $V_{\mathrm{eff}}^{(3)}$ terms have smaller prefactors for $a_2^{(2)}$ and $a_4^{(2)}$.

The corrections to a molecular property, P for the vibrational motion is given as

$$\langle P \rangle = \frac{\langle \Psi | P(q) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \ , \tag{27}$$

where the property surface P_{E} may be expanded around an expansion point r_{exp} as

$$P(q) = \sum_m P_m = P_{\mathrm{exp}}^{(0)} + P_{\mathrm{exp}}^{(1)} q + \frac{1}{2} P_{\mathrm{exp}}^{(2)} q^2 + \frac{1}{6} P_{\mathrm{exp}}^{(3)} q^3 + \frac{1}{24} P_{\mathrm{exp}}^{(4)} q^4 + \cdots \ . \tag{28}$$

Applying the perturbation–variation expansion to the expansion in Eq. (28), one obtains [18]

$$\langle P \rangle = \sum_{mn}^{\infty} \langle P_m^{(n)} \rangle \ , \tag{29}$$

where

$$\langle P_m^{(n)} \rangle = \left[\sum_{k=0}^{\infty} \langle \lambda^k \Psi^{(k)} | P_m | \lambda^{n-k} \Psi^{(n-k)} \rangle \right] \times \left[1 + \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} (-1)^m \left(\langle \lambda^l \Psi^{(l)} | \lambda^l \Psi^{(l)} \rangle \right)^m \right] \ , \tag{30}$$

where we have carried out a Taylor expansion of the normalization $\langle \Psi | \Psi \rangle^{-1}$ around $\Psi = \Psi^{(0)}$. The zeroth-order term in λ gives

$$\langle P^{(0)} \rangle_{\mathrm{exp}} = \langle P_0^{(0)} \rangle_{\mathrm{exp}} + \langle P_2^{(0)} \rangle_{\mathrm{exp}} + \langle P_4^{(0)} \rangle_{\mathrm{exp}} = P_{\mathrm{exp}}^{(0)} + \frac{P_{\mathrm{exp}}^{(2)}}{4m\omega_{\mathrm{exp}}} + \frac{P_{\mathrm{exp}}^{(4)}}{32\left(m\omega_{\mathrm{exp}}\right)^2} \ . \tag{31}$$

The first-order term in λ gives

$$\langle P^{(1)} \rangle_{\mathrm{exp}} = \langle P_1^{(1)} \rangle_{\mathrm{exp}} + \langle P_3^{(1)} \rangle_{\mathrm{exp}} = \sqrt{\frac{2}{m\omega_{\mathrm{exp}}}} P_{\mathrm{exp}}^{(1)} a_1^{(1)} + \frac{P_{\mathrm{exp}}^{(3)}}{6\left(m\omega_{\mathrm{exp}}\right)^{\frac{3}{2}}} \sqrt{\frac{3}{2}} \left(\sqrt{3} a_1^{(1)} + \sqrt{2} a_3^{(1)} \right) \ . \tag{32}$$

If the expansion is carried out around the specific point r_{eff}, $\langle P^{(1)} \rangle$ is reduced to

$$\langle P^{(1)} \rangle_{\mathrm{eff}} = \frac{P_{\mathrm{eff}}^{(3)}}{6(m\omega_{\mathrm{eff}})^{\frac{3}{2}}} \sqrt{3} a_3^{(1)} \ , \tag{33}$$

i.e., the term that includes the gradient of the property vanishes. Hence, the most important first-order contribution, $\langle P_1^{(1)} \rangle$, and the largest contribution to $\langle P_3^{(1)} \rangle$ vanish if a variationally determined expansion point is adopted.

---

[1] Equations (17) and (18) are consistent with Eqs. (22) and (23) of Ref. [18] for polyatomic molecules. The differences are due to the fact that we have carried out a Taylor expansion of the potential instead of a power expansion, and that we have used the coordinate q instead of $\xi = \sqrt{m\omega}q$

We note that the traditional perturbation approach, also including the anharmonicity of the potential [23, 24], corresponds to the inclusion of $\langle P_2^{(0)} \rangle_{\mathrm{e}}$ and $\langle P_1^{(1)} \rangle_{\mathrm{e}}$.

The first contribution to which higher-order terms in the normalization contribute is the term of second-order in λ, for which we get

$$\begin{aligned} \langle P_m^{(2)} \rangle &= 2\langle \Psi^{(0)} | P_m | \Psi^{(2)} \rangle + \langle \Psi^{(1)} | P_m | \Psi^{(1)} \rangle \\ &\quad - \langle \Psi^{(0)} | P_m | \Psi^{(0)} \rangle \langle \Psi^{(1)} | \Psi^{(1)} \rangle \ . \end{aligned} \tag{34}$$

We note that $\langle P_0^{(2)} \rangle$ is zero since the second and third terms cancel each other. Hence, we get

$$\begin{aligned} \langle P_2^{(2)} \rangle_{\mathrm{exp}} = \frac{1}{2m\omega_{\mathrm{exp}}} P_{\mathrm{exp}}^{(2)} \Big(& \sqrt{2} a_2^{(2)} + a_1^{(1)} a_1^{(1)} \\ & + \sqrt{6} a_1^{(1)} a_3^{(1)} + 3 a_3^{(1)} a_3^{(1)} \Big) \end{aligned} \tag{35}$$

and

$$\begin{aligned} \langle P_4^{(2)} \rangle_{\mathrm{exp}} = \frac{1}{24 \left(m\omega_{\mathrm{exp}} \right)^2} P_{\mathrm{exp}}^{(4)} \Bigg(& \frac{3}{\sqrt{2}} a_2^{(2)} + \sqrt{\frac{3}{2}} a_4^{(2)} \\ & + 3 a_1^{(1)} a_1^{(1)} + 5\sqrt{6} a_1^{(1)} a_3^{(1)} + 18 a_3^{(1)} a_3^{(1)} \Bigg) \ , \end{aligned} \tag{36}$$

which are simplified if the expansion is carried out around r_{eff} since $a_1^{(1)}$ is then zero, and we may then write

$$\langle P_2^{(2)} \rangle_{\mathrm{eff}} = \frac{1}{2m\omega_{\mathrm{eff}}} P_{\mathrm{eff}}^{(2)} \left(\sqrt{2} a_2^{(2)} + 3 a_3^{(1)} a_3^{(1)} \right) \tag{37}$$

and

$$\begin{aligned} \langle P_4^{(2)} \rangle_{\mathrm{eff}} &= \frac{1}{24 (m\omega_{\mathrm{eff}})^2} \\ &\quad \times P_{\mathrm{eff}}^{(4)} \left(\frac{3}{\sqrt{2}} a_2^{(2)} + \sqrt{\frac{3}{2}} a_4^{(2)} + 18 a_3^{(1)} a_3^{(1)} \right) \ . \end{aligned} \tag{38}$$

In Eq. (33) it was found that the term including the gradient of the property vanishes for the first order in λ if r_{eff} is used as an expansion point. This is in accordance with the observation that if the expansion point is chosen as the vibrationally averaged geometry ($r_{\mathrm{exp}} = \langle r \rangle$), the linear term of $P(q)$ in Eq. (28) will not contribute to $\langle P \rangle$ since $\langle q \rangle = \langle r - \langle r \rangle \rangle$ trivially becomes zero [25]. Furthermore, it is noted that the second-order contributions in Eqs. (35) and (36) do not contribute to the averaged molecular geometry since they do not include the gradient of the property. Consequently, the choice of r_{eff} as an expansion point corresponds to the vibrationally averaged geometry to second order in the wave function. By calculating the average molecular geometry, $\langle r \rangle$, from Eqs. (31) and (32) by adopting an expansion around r_{e}, we obtain

$$\langle r \rangle = r_{\mathrm{e}} - \frac{V_{\mathrm{e}}^{(3)}}{4\omega_{\mathrm{e}} (m\omega_{\mathrm{e}})^2} \ , \tag{39}$$

which is equal to r_{eff} to second order in λ. We can thus use Eq. (39) to calculate r_{eff} and it is therefore not necessary to carry out the minimization in Eq. (7).

3 Computational details

We used the DALTON program [26] to calculate potential and property surfaces for HF, HCl, N_2 and F_2. Since our purpose is to study the convergence properties of the perturbation approach to rovibrational corrections rather than to calculate accurate vibrationally averaged properties, we restricted ourselves to calculations at the self-consistent-field (SCF) level. The molecules studied have different harmonic frequencies and anharmonicities and also have different geometry dependencies of the property surfaces. For all molecules, we calculated magnetizabilities [27], rotational g factors [28], nuclear shielding constants [29] and spin-rotation constants [28], using London atomic orbitals to ensure gauge-origin independence and size-extensivity [30]. We did not include the Thomas precession contribution to the spin-rotation constants. For the polar molecules HF and HCl, we have also reported the calculated dipole moments. In all calculations we used the atomic natural orbitals (ANO) basis sets of Pierloot et al. [31], with a [5*s*4*p*3*d*] contraction for Cl, [4*s*3*p*2*d*] for N and F and [3*s*2*p*] for H. To analyze the potential and property surfaces, we used MATLAB [32]. For calibration, the rovibrational corrections were calculated numerically using a finite-element approach previously used to calculate rovibrational corrections to nuclear magnetic shieldings and spin-rotation constants [1, 2].

4 Results

For all molecules, the zero-point vibrationally averaged properties were calculated both using an expansion around the equilibrium geometry (denoted with the subscript e) and from an expansion around the effective geometry defined in Eq. (7) (denoted with the subscript eff). The parameters that describe the potential functions are reported in Table 1.

For the HF molecule, the effective bond length, r_{eff}, is a few hundredths of a bohr longer than the equilibrium value, r_{e}. For the dipole moment of HF (see Table 2 for

Table 1. Potential function parameters (in atomic units)

	HF	HCl	N_2	F_2
r_{e}	1.6988	2.3899	2.0172	2.5210
$V_{\mathrm{e}}^{(2)}$	0.7259	0.3646	1.9723	0.5754
ω_{e}	0.02040	0.01429	0.01243	0.00576
$V_{\mathrm{e}}^{(3)}$	−2.7639	−1.0517	−7.1231	−1.8558
$V_{\mathrm{e}}^{(4)}$	9.7657	2.7764	22.1405	5.1322
$a_1^{(1)}$	0.1128	0.1010	0.0507	0.0571
$a_3^{(1)}$	0.0307	0.0275	0.0138	0.0155
$a_2^{(2)}$	0.0103	0.00843	0.00232	0.00296
$a_4^{(2)}$	0.00730	0.00590	0.00154	0.00196
$a_6^{(2)}$	0.00211	0.00169	0.000426	0.000539
r_{eff}	1.7258	2.4184	2.0229	2.5291
$V_{\mathrm{eff}}^{(1)}$	0.0186	0.00997	0.0111	0.00460
$V_{\mathrm{eff}}^{(2)}$	0.6548	0.3357	1.9320	0.5605
ω_{eff}	0.01937	0.01371	0.01230	0.00569
$V_{\mathrm{eff}}^{(3)}$	−2.5137	−0.9756	−6.9979	−1.8147
$V_{\mathrm{eff}}^{(4)}$	8.7898	2.5735	21.7406	5.0117
$a_3^{(1)}$	0.0318	0.0283	0.0139	0.0157
$a_2^{(2)}$	−0.0111	−0.00876	−0.00194	−0.00244
$a_4^{(2)}$	0.000496	0.000406	0.000152	0.000199
$a_6^{(2)}$	0.00226	0.00179	0.000432	0.000551

Table 2. Property function parameters of HF

	μ (a.u.)	ξ (10^{-30} J/T^2)	$\Delta\xi$ (10^{-30} J/T^2)	g	σ^{F} (ppm)	$\Delta\sigma^{\mathrm{F}}$ (ppm)	σ^{H} (ppm)	$\Delta\sigma^{\mathrm{H}}$ (ppm)	M^{F} (kHz)	M^{H} (kHz)
$P_{\mathrm{e}}^{(0)}$	0.7483	−172.651	8.1311	0.7677	420.547	91.9344	29.7286	23.7437	−287.847	80.2449
$P_{\mathrm{e}}^{(1)}$	0.4119	−18.8974	1.9817	−0.2380	−204.988	304.028	−25.4640	−28.7552	−809.644	−235.992
$P_{\mathrm{e}}^{(2)}$	0.1121	33.2209	−40.1752	−0.2994	−372.642	568.076	42.8597	28.8797	2.7227	808.393
$P_{\mathrm{e}}^{(3)}$	−0.2896	21.5739	−37.9111	0.7021	−396.602	570.864	−75.3014	−21.3590	−528.691	−3032.60
$P_{\mathrm{e}}^{(4)}$	0.8362	7.1616	22.4817	−2.0259	12.2207	46.628	101.568	24.8298	2491.39	12451.5
$\langle P_2^{(0)}\rangle_{\mathrm{e}}$	0.000787	0.2334	−0.2822	−0.00210	−2.6178	3.9907	0.3011	0.2029	0.0191	5.6789
$\langle P_4^{(0)}\rangle_{\mathrm{e}}$	0.000021	0.000177	0.000555	−0.000050	−0.000302	0.00115	0.00251	0.000613	0.0615	0.3072
$\langle P_1^{(1)}\rangle_{\mathrm{e}}$	0.01102	−0.5054	0.0530	−0.00636	−5.4825	8.1313	−0.6810	−0.7691	−21.654	−6.3117
$\langle P_3^{(1)}\rangle_{\mathrm{e}}$	−0.000067	0.00495	−0.00871	0.000161	−0.0911	0.1311	−0.0173	−0.00490	−0.1214	−0.6964
$\langle P_2^{(2)}\rangle_{\mathrm{e}}$	0.000061	0.0180	−0.0218	−0.000162	−0.2021	0.3081	0.0232	0.0157	0.00148	0.4384
$\langle P_4^{(2)}\rangle_{\mathrm{e}}$	0.000004	0.000037	0.000118	−0.000011	0.000064	0.000244	0.00053	0.000130	0.0130	0.0652
$\langle P\rangle_{\mathrm{e}}$	0.7601	−172.900	7.8720	0.7592	412.154	104.497	29.3576	23.1890	−309.528	79.7266
$P_{\mathrm{eff}}^{(0)}$	0.7595	−173.149	8.1698	0.7612	414.876	100.351	29.0565	22.9779	−309.706	74.1588
$P_{\mathrm{eff}}^{(1)}$	0.4149	−17.9926	0.8833	−0.2458	−215.193	319.572	−24.3340	−27.9833	−809.755	−215.233
$P_{\mathrm{eff}}^{(2)}$	0.1046	33.8058	−41.1903	−0.2811	−383.342	583.500	40.8629	28.3124	−10.6603	730.861
$P_{\mathrm{eff}}^{(3)}$	−0.2661	21.7455	−37.2805	0.6522	−395.997	571.628	−72.6573	−20.6676	−463.446	−2718.19
$P_{\mathrm{eff}}^{(4)}$	0.8990	5.7179	23.8463	−1.6883	31.4095	11.8345	94.7701	25.9378	2337.02	10883.2
$\langle P_2^{(0)}\rangle_{\mathrm{eff}}$	0.000774	0.2501	−0.3047	−0.00208	−2.8355	4.3161	0.3023	0.2094	−0.0789	5.4061
$\langle P_4^{(0)}\rangle_{\mathrm{eff}}$	0.000025	0.000156	0.000652	−0.000046	−0.000859	0.000324	0.00259	0.000710	0.0639	0.2977
$\langle P_3^{(1)}\rangle_{\mathrm{eff}}$	−0.000012	0.00102	−0.00174	0.000030	−0.0185	0.0267	−0.00339	−0.000965	−0.0216	−0.1269
$\langle P_2^{(2)}\rangle_{\mathrm{eff}}$	−0.000020	−0.00636	0.00775	0.000053	0.0721	−0.1097	−0.00768	−0.00532	0.00200	−0.1374
$\langle P_4^{(2)}\rangle_{\mathrm{eff}}$	−0.0000009	−0.000058	−0.000024	0.000002	−0.000032	−0.000012	−0.000097	−0.000026	−0.00237	−0.0111
$\langle P\rangle_{\mathrm{eff}}$	0.7602	−172.904	7.8718	0.7592	412.095	104.584	29.3502	23.1817	−309.743	79.5872
$\langle P\rangle_{\mathrm{num}}^{\mathrm{a}}$	0.7602	−172.904	7.8715	0.7591	412.095	104.584	29.3510	23.1820	−309.738	79.6031

[a] Obtained by numerical methods

the properties of HF), this shift in bond length gives a vibrational contribution of 0.0112 a.u., whereas the harmonic term $\langle\mu_2^{(0)}\rangle$ gives the dominating contribution to the remaining 0.0007 a.u. In the vicinity of r_{e}, the dipole moment of HF thus changes almost linearly with the bond length.

For the magnetizability, ξ, the zero-point vibrational contribution behaves differently. The isotropic part has a very small vibrational contribution of about -0.25×10^{-30} J/T^2, to be compared with the equilibrium value of -172.65×10^{-30} J/T^2, which is due both to the fact that each contribution to the vibrational average is small, but also because the two largest terms cancel each other. For the magnetizability anisotropy, $\Delta\xi$, the harmonic term $\langle\Delta\xi_2^{(0)}\rangle$ is the dominant contribution. Whereas the shift in the geometry gives a small positive contribution, $\langle\Delta\xi_2^{(0)}\rangle$ gives a much larger negative contribution. As for the dipole moment, $\langle P_4^{(0)}\rangle$ and $\langle P_3^{(1)}\rangle$, as well as the terms of second order in λ, give contributions which are orders of magnitudes smaller than the largest terms. We note in particular that $\langle P_3^{(1)}\rangle_{\mathrm{eff}}$ is much smaller than $\langle P_3^{(1)}\rangle_{\mathrm{e}}$, which is due to the fact that $a_1^{(1)}$ is zero for the expansion around the effective geometry. The same behavior is found for the terms of second order in λ. Compared to numerical integration, both perturbation approaches give excellent results. As expected, the expansion around an effective geometry gives results closer to numerical integration than an expansion around the equilibrium geometry, which is mainly due to the vanishing $a_1^{(1)}$ term in the former case.

For the isotropic nuclear magnetic shieldings, σ^{F} and σ^{H}, as well as for their anisotropies, $\Delta\sigma^{\mathrm{F}}$ and $\Delta\sigma^{\mathrm{H}}$, the shift in the geometry and the harmonic term $\langle P_2^{(0)}\rangle$ are the dominant contributions to the rovibrational correction. For the fluorine spin-rotation constant, M^{F}, the shift in the geometry gives almost all the vibrational effects, whereas $\langle P_1^{(1)}\rangle_{\mathrm{e}}$ and $\langle P_2^{(0)}\rangle_{\mathrm{e}}$ almost cancel for M^{H}. In this case, $\langle P_2^{(2)}\rangle_{\mathrm{e}}$, $\langle P_3^{(1)}\rangle_{\mathrm{e}}$ and $\langle P_4^{(0)}\rangle_{\mathrm{e}}$ also give substantial contributions to $\langle M^{\mathrm{H}}\rangle$.

As for HF, the effective bond length in HCl is only a few hundredths of a bohr longer than that of the equilibrium geometry (Table 1). Both the second ($V_{\mathrm{e}}^{(2)}$) and third ($V_{\mathrm{e}}^{(3)}$) derivatives with respect to the geometry are, however, much smaller for HCl than for HF, which is also reflected in the smaller vibrational frequency. We note that the same trends applies to the properties of the HCl molecule as applied for HF (see Table 3 for the results obtained for HCl), as for instance the dipole moment changes almost linearly with the bond length. For the isotropic part of the magnetizability, the zero-point vibrational contribution is small because the effects of the geometry shift and the harmonic term $\langle\xi_2^{(0)}\rangle$ almost cancel. As for HF, the vibrational effects on the magnetizability anisotropy, $\langle \Delta\xi \rangle_{\mathrm{eff}}$, are dominated by the harmonic term $\langle \Delta\xi_2^{(0)} \rangle$. For the nuclear shielding and spin-rotation constants, we note that the two leading terms $\langle P_1^{(1)} \rangle_{\mathrm{e}}$ (or the shift of the geometry) and $\langle P_2^{(0)} \rangle$ dominate.

Compared to HF and HCl, N_2 has a much larger reduced mass, reflected in a small harmonic vibrational frequency as well as small contributions to the first-order wave function (Table 1). Furthermore, the difference between the effective and equilibrium geometries is only about 0.006 bohr. Still, the zero-point vibrational effects on the magnetizability (Table 4) are much larger for N_2 than for HF and HCl because the two leading terms, $\langle P_1^{(1)} \rangle_{\mathrm{e}}$ and $\langle P_2^{(0)} \rangle$, have the same sign for N_2, whereas they almost canceled for HF and HCl. For the rotational g factor, the shielding tensor and the spin-rotation constant, we again note that the dominant zero-point vibrational contributions stem from the shift in the bond length and the harmonic contribution. In particular for the shielding tensor, the small change in the geometry contributes several parts per million to the rovibrational correction. For N_2, the perturbation expansion gives larger deviations from numerical integration than was the case for HF and HCl. For some properties, the expansion around r_{eff} gives larger deviations compared to numerical integration than does an expansion around r_{e}, which indicate that higher-order terms are more important for this molecule.

The geometry shift of F_2 is 0.008 bohr, which is slightly larger than that of N_2. Furthermore, F_2 has a much smaller harmonic frequency and third derivative of the potential. As for N_2, the vibrational contributions to the magnetizability tensor are a few 10^{-30} J/T^2 (Table 5). Thus, for the four molecules studied here, the vibrational contributions to the isotropic part of the magnetizability are all less than 1%. The shielding tensor of F_2 has a large geometry dependence, but also a substantial contribution from the harmonic term. In fact, the isotropic shielding is 17.8 ppm at the equilibrium geometry, but the small shift in the geometry of only 0.008 bohr to the effective geometry decreases the shielding to 9.0 ppm, and the harmonic term decreases σ^{F} further to 4.0 ppm. As for HF and HCl, the perturbation expansions give results close to that of numerical integration.

5 Discussion

As discussed in the previous section, both an expansion around the equilibrium geometry and the effective geometry determined by Eq. (7) give results that in most cases are in good agreement with those obtained using numerical integration when all contributions to second order in λ are included. However, we also want to investigate the performance and adequacy of using

Table 3. Property function parameters of HCl

	μ (a.u)	ξ (10^{-30} J/T^2)	$\Delta\xi$ (10^{-30} J/T^2)	g	σ^{Cl} (ppm)	$\Delta\sigma^{\mathrm{Cl}}$ (ppm)	σ^{H} (ppm)	$\Delta\sigma^{\mathrm{H}}$ (ppm)	M^{Cl} (kHz)	M^{H} (kHz)
$P_{\mathrm{e}}^{(0)}$	0.4563	−411.488	−4.9392	0.4692	968.716	270.436	31.3338	22.2135	−50.3732	43.1303
$P_{\mathrm{e}}^{(1)}$	0.2294	−22.0584	0.8982	−0.0736	−330.118	494.048	−17.8783	−19.3556	−52.9983	−83.7721
$P_{\mathrm{e}}^{(2)}$	0.0896	46.2514	−63.3254	−0.4472	−456.684	687.509	21.1457	13.3702	−25.7732	197.797
$P_{\mathrm{e}}^{(3)}$	−0.1016	34.5145	−38.3476	0.7029	−373.656	553.879	−29.1295	−3.2633	12.5265	−537.359
$P_{\mathrm{e}}^{(4)}$	0.1081	−12.1140	10.2883	−1.5239	−77.7689	134.169	38.4488	−9.3522	−10.6118	1631.78
$\langle P_2^{(0)} \rangle_{\mathrm{e}}$	0.000878	0.4532	−0.6205	−0.00438	−4.4748	6.7365	0.2072	0.1310	−0.2525	1.9381
$\langle P_4^{(0)} \rangle_{\mathrm{e}}$	0.000005	−0.00058	0.00049	−0.000073	−0.00373	0.00644	0.00185	−0.000449	−0.00051	0.0783
$\langle P_1^{(1)} \rangle_{\mathrm{e}}$	0.00649	−0.6235	0.0254	−0.00208	−9.3316	13.9656	−0.5054	−0.5471	−1.4981	−2.3680
$\langle P_3^{(1)} \rangle_{\mathrm{e}}$	−0.000034	0.0117	−0.0130	0.000238	−0.1265	0.1875	−0.00986	−0.00110	0.00424	−0.1819
$\langle P_2^{(2)} \rangle_{\mathrm{e}}$	0.000055	0.0283	−0.0387	−0.000273	−0.2791	0.4201	0.0129	0.00817	−0.0157	0.1209
$\langle P_4^{(2)} \rangle_{\mathrm{e}}$	0.0000009	−0.000100	0.000085	−0.000013	−0.000639	0.00110	0.000316	−0.000077	−0.000087	0.0134
$\langle P \rangle_{\mathrm{e}}$	0.4637	−411.619	−5.5854	0.4626	954.500	291.753	31.0408	21.8039	−52.1360	42.7311
$P_{\mathrm{eff}}^{(0)}$	0.4629	−412.097	−4.9394	0.4669	959.129	284.786	30.8331	21.6677	−51.8929	40.8229
$P_{\mathrm{eff}}^{(1)}$	0.2320	−20.7273	−0.9206	−0.0860	−343.274	513.851	−17.2878	−18.9762	−53.7272	−78.3512
$P_{\mathrm{eff}}^{(2)}$	0.0868	47.2295	−64.4137	−0.4278	−467.358	703.338	20.3317	13.2734	−25.4210	183.136
$P_{\mathrm{eff}}^{(3)}$	−0.0982	34.1813	−38.1030	0.6613	−376.029	557.927	−28.0415	−3.5389	12.1957	−493.067
$P_{\mathrm{eff}}^{(4)}$	0.1314	−11.2193	6.7781	−1.3979	−89.5324	151.084	37.9574	−9.9786	−12.7675	1481.60
$\langle P_2^{(0)} \rangle_{\mathrm{eff}}$	0.000886	0.4822	−0.6577	−0.00437	−4.7721	7.1816	0.2076	0.1355	−0.2596	1.8700
$\langle P_4^{(0)} \rangle_{\mathrm{eff}}$	0.000007	−0.00058	−0.000353	−0.000073	−0.00467	0.00788	0.00198	−0.000520	−0.000666	0.0772
$\langle P_3^{(1)} \rangle_{\mathrm{eff}}$	−0.000007	0.00230	−0.00257	0.000045	−0.0253	0.0376	−0.00189	−0.000238	−0.000821	−0.0332
$\langle P_2^{(2)} \rangle_{\mathrm{eff}}$	−0.000018	−0.00963	0.0131	0.000087	0.0953	−0.1434	−0.00415	−0.00271	0.00518	−0.0374
$\langle P_4^{(2)} \rangle_{\mathrm{eff}}$	−0.0000002	0.000017	−0.000010	0.000002	0.000136	−0.000229	−0.000058	0.000015	0.000019	−0.00224
$\langle P \rangle_{\mathrm{eff}}$	0.4638	−411.623	−5.5862	0.4626	954.422	291.869	31.0366	21.7998	−52.1471	42.6973
$\langle P \rangle_{\mathrm{num}}$	0.4638	−411.623	−5.5858	0.4626	954.435	291.856	31.0367	21.8000	−52.1463	42.6970

Table 4. Property function parameters of N_2

	ξ (10^{-30} J/T^2)	$\Delta\xi$ (10^{-30} J/T^2)	g	σ^N (ppm)	$\Delta\sigma^N$ (ppm)	M^N (kHz)
$P_e^{(0)}$	−212.147	−135.826	−0.2782	−67.2001	610.899	−14.0354
$P_e^{(1)}$	133.017	−296.185	−0.1982	−518.626	745.690	−8.0401
$P_e^{(2)}$	502.918	−706.320	−0.7313	−1049.06	1619.93	−20.8790
$P_e^{(3)}$	1196.59	−1791.20	−0.6027	−2890.21	4257.37	−42.7261
$P_e^{(4)}$	6321.65	−9610.88	−11.2460	−15768.6	23791.0	−380.368
$\langle P_2^{(0)}\rangle_e$	0.7924	−1.1130	−0.00115	−1.6530	2.5525	−0.0329
$\langle P_4^{(0)}\rangle_e$	0.00785	−0.0119	−0.000014	−0.0196	0.0295	−0.000472
$\langle P_1^{(1)}\rangle_e$	0.7570	−1.6855	−0.00113	−2.9514	4.2435	−0.0458
$\langle P_3^{(1)}\rangle_e$	0.0131	−0.0196	−0.000007	−0.0317	0.0467	−0.000468
$\langle P_2^{(2)}\rangle_e$	0.0129	−0.0181	−0.000019	−0.0269	0.0415	−0.000535
$\langle P_4^{(2)}\rangle_e$	0.000349	−0.000530	−0.0000006	−0.00087	0.00131	−0.000021
$\langle P\rangle_e$	−210.563	−138.675	−0.2805	−71.8835	617.814	−14.1155
$P_{eff}^{(0)}$	−211.380	−137.529	−0.2793	−70.1778	615.182	−14.0816
$P_{eff}^{(1)}$	135.908	−300.247	−0.2024	−524.662	755.007	−8.1600
$P_{eff}^{(2)}$	509.851	−716.701	−0.7350	−1065.81	1644.62	−21.1291
$P_{eff}^{(3)}$	1232.69	−1846.07	−0.6666	−2980.19	4393.12	−44.8860
$P_{eff}^{(4)}$	6324.90	−9615.81	−11.1485	−15753.5	23767.6	−376.372
$\langle P_2^{(0)}\rangle_{eff}$	0.8117	−1.1410	−0.00117	−1.6968	2.6183	−0.0336
$\langle P_4^{(0)}\rangle_{eff}$	0.00802	−0.0122	−0.000014	−0.0200	0.0301	−0.000477
$\langle P_3^{(1)}\rangle_{eff}$	0.00251	−0.00377	−0.000001	−0.00608	0.00896	−0.000092
$\langle P_2^{(2)}\rangle_{eff}$	−0.00350	0.00492	0.000005	0.00732	−0.0113	0.000145
$\langle P_4^{(2)}\rangle_{eff}$	−0.000047	0.000071	0.00000008	0.00012	−0.00018	0.000003
$\langle P\rangle_{eff}$	−210.561	−138.681	−0.2805	−71.8932	617.828	−14.1157
$\langle P\rangle_{num}$	−210.574	−138.660	−0.2805	−71.8602	617.779	−14.1151

Eq. (1) to calculate rovibrational corrections, i.e., using a simple harmonic oscillator approximation.

In Table 6 we have collected the percentage of the zero-point vibrational contribution recovered by using Eq. (1), i.e., $P_{eff}^{(0)} + \langle P_2^{(0)}\rangle_{eff} - P_e^{(0)}$, relative to the zero-point vibrational contribution estimated using numerical integration, $\langle P\rangle - P_e^{(0)}$. In this table we also include the more common approach of obtaining zero-point vibrational averaging by expanding around the equilibrium geometry, also including the anharmonicity of the potential, i.e., $\langle P_2^{(0)}\rangle_e + \langle P_1^{(1)}\rangle_e$. We also indicate the size of the numerical zero-point vibrational contribution relative to the total rovibrationally corrected molecular property.

From Table 6 one notes that by using Eq. (1) very good results are in general obtained, with most zero-point vibrational contributions being reproduced to within a couple of a percent, although a few exceptions do exist, most notably the hydrogen shieldings. We also note that the use of a harmonic oscillator approximation at the effective geometry gives more accurate results than does an expansion around the equilibrium geometry, even when the anharmonicity of the potential is included in the latter approach. In particular, the use of the effective geometry as an expansion point gives significantly better estimates of the rovibrational corrections than does the use of the equilibrium geometry for the HCl molecule.

The observation that we get very accurate estimates of zero-point vibrational corrections by using an effective geometry indicates that this approach may also be viable for estimating rovibrational corrections in polyatomic molecules. Not only does the approach appear to give very good zero-point vibrational correction, but the simple form of the nuclear wave function in this approximation, a simple Gaussian function, makes it easy to construct vibrational wave functions also for polyatomic molecules. It should be emphasized that r_{eff} is equal to the vibrationally averaged molecular geometry, $\langle r\rangle$, to second order in λ, and it has thus been demonstrated that an expansion around $\langle r\rangle$ converges faster than an expansion around r_e. Furthermore, the parameters obtained in an expansion around $\langle r\rangle$, (r_{eff}), correspond to physically meaningful parameters. However, the accuracy of this approach in polyatomic molecules will need further investigation.

6 Conclusions

In this work, we have demonstrated that we can, by regarding the zero-point vibrational energy as a potential, make a perturbation expansion of the nuclear wave function that converges more rapidly than an expansion around the equilibrium geometry. Even if the shift of the

Table 5. Property function parameters of F_2

	ξ (10^{-30} J/T^2)	$\Delta\xi$ (10^{-30} J/T^2)	g	σ^F (ppm)	$\Delta\sigma^F$ (ppm)	M^F (kHz)
$P_e^{(0)}$	−207.169	−105.900	−0.0822	17.7513	708.096	−99.1259
$P_e^{(1)}$	84.7921	−149.979	−0.0419	−1073.33	1594.34	−202.723
$P_e^{(2)}$	362.936	−525.362	−0.3631	−1937.34	2925.74	−140.438
$P_e^{(3)}$	320.795	−485.063	0.4909	−2943.68	4387.63	−233.723
$P_e^{(4)}$	1164.3	−1817.19	−2.4026	−6577.02	9906.61	−691.517
$\langle P_2^{(0)}\rangle_e$	0.9090	−1.3158	−0.000909	−4.8522	7.3277	−0.3517
$\langle P_4^{(0)}\rangle_e$	0.00365	−0.00570	−0.000007	−0.0206	0.0311	−0.00217
$\langle P_1^{(1)}\rangle_e$	0.6849	−1.2115	−0.000338	−8.6703	12.8789	−1.6376
$\langle P_3^{(1)}\rangle_e$	0.00793	−0.0120	0.000012	−0.0728	0.1085	−0.00578
$\langle P_2^{(2)}\rangle_e$	0.0188	−0.0272	−0.000019	−0.1003	0.1515	−0.00727
$\langle P_4^{(2)}\rangle_e$	0.000206	−0.000322	−0.0000004	−0.00116	0.00175	−0.000122
$\langle P\rangle_e$	−205.544	−108.473	−0.0835	4.0339	728.596	−101.131
$P_{eff}^{(0)}$	−206.470	−107.132	−0.0826	8.9930	721.107	−100.773
$P_{eff}^{(1)}$	87.7426	−154.251	−0.0448	−1089.13	1618.18	−203.869
$P_{eff}^{(2)}$	365.573	−529.351	−0.3592	−1961.40	2961.61	−142.354
$P_{eff}^{(3)}$	330.281	−499.854	0.4716	−2997.41	4468.57	−239.332
$P_{eff}^{(4)}$	1177.89	−1834.95	−2.3538	−6691.47	10077.7	−693.408
$\langle P_2^{(0)}\rangle_{eff}$	0.9277	−1.3433	−0.000911	−4.9772	7.5153	−0.3612
$\langle P_4^{(0)}\rangle_{eff}$	0.00379	−0.00591	−0.000008	−0.0215	0.0324	−0.00223
$\langle P_3^{(1)}\rangle_{eff}$	0.00153	−0.00232	0.000002	−0.0139	0.0207	−0.00111
$\langle P_2^{(2)}\rangle_{eff}$	−0.00504	0.00730	0.000005	0.0270	−0.0408	0.00196
$\langle P_4^{(2)}\rangle_{eff}$	−0.000028	0.000043	0.00000006	0.000157	−0.000236	0.000016
$\langle P\rangle_{eff}$	−205.542	−108.477	−0.0835	4.0076	728.635	−101.135
$\langle P\rangle_{num}$	−205.542	−108.477	−0.0835	4.0074	728.635	−101.135

Table 6. The recovery of the numerical zero-point vibrational (ZPV) contribution to the different molecular properties using Eq. (1) or calculated using the equilibrium geometry as an expansion, including the anharmonicity of the potential (see text). All numbers in percent

Molecule	Exp. point	μ	ξ	$\Delta\xi$	g	σ^X	$\Delta\sigma^X$	σ^H	$\Delta\sigma^H$	M^X	M^H
HF	Effective[a]	100.6	98.0	102.5	99.8	100.6	100.7	97.9	99.1	100.2	106.0
	Equilibrium[b]	99.2	107.5	88.3	98.4	95.8	95.8	100.6	100.8	98.8	98.6
	ZPV contribution[c]	1.6	0.1	3.3	1.1	2.1	12.1	1.3	2.4	7.1	0.8
HCl	Effective[a]	99.8	93.9	101.7	101.1	100.5	100.5	98.7	99.2	100.3	100.9
	Equilibrium[b]	98.2	126.1	92.0	97.9	96.7	96.6	100.4	100.6	98.7	99.2
	ZPV contribution[c]	1.6	0.03	11.5	1.4	1.5	7.3	1.0	1.9	3.4	1.0
N_2	Effective[a]		100.4	100.4	98.7	100.3	100.3			100.1	
	Equilibrium[b]		98.4	98.7	99.1	98.8	98.8			98.7	
	ZPV contribution[c]		0.7	2.0	0.8	6.5	1.1			0.6	
F_2	Effective[a]		100.0	99.9	100.8	99.9	99.9			100.0	
	Equilibrium[b]		98.1	98.1	95.9	98.4	98.4			99.0	
	ZPV contribution[c]		0.8	2.4	1.6	343	2.8			2.0	

[a] Calculated as $\left[\left(P_{eff}^{(0)} + \langle P_2^{(0)}\rangle_{eff} - P_e^{(0)}\right)/\left(\langle P\rangle_{num} - P_e^{(0)}\right)\right] \times 100\%$

[b] Calculated as $\left[\left(\langle P_2^{(0)}\rangle_e + \langle P_1^{(1)}\rangle\right)/\left(\langle P\rangle_{num} - P_e^{(0)}\right)\right] \times 100\%$

[c] Calculated as $\left[\left(\langle P\rangle_{num} - P_e^{(0)}\right)/\langle P\rangle_{num}\right] \times 100\%$

geometry is only a few hundredths of a bohr for HF and HCl, and less than 0.01 bohr for N_2 and F_2, these shifts have large effects on the zero-point vibrational corrections, especially on the shielding tensors. Furthermore, we have shown that Eq. (1) gives the dominant vibrational effects, and that the sizes of the higher-order contributions are, in general, much smaller than the errors introduced in an electron structure calculation when the orbital or correlation spaces are truncated [12–15]. Although the traditional perturbation expansion around the equilibrium geometry [23, 24] gives accurate results, we have shown that if the expansion is carried out around the effective geometry instead, the largest contribution to $\langle P_3^{(1)}\rangle$, $\langle P_2^{(2)}\rangle$ and $\langle P_4^{(2)}\rangle$ vanishes, in contrast to the case if the expansion is carried out around the equilibrium geometry.

Acknowledgement. K.R. has been supported by the Norwegian Research Council through a postdoctoral fellowship from the Norwegian Research Council (grant no. 125851/410).

References

1. Sundholm D, Gauss J, Schäfer A (1996) J Chem Phys 105: 11051–11059
2. Sundholm D, Gauss J (1997) Mol Phys 92: 1007–1014
3. Jensen P, Paidarova I, Spriko V, Sauer SPA (1997) Mol Phys 91: 319–332
4. Bludský O, Jensen P (1997) Mol Phys 91: 653–662
5. Osmann G, Bunker PR, Jensen P, Kraemer WP (1997) Chem Phys 225: 33–54
6. Malmqvist P-Å, Lindh R, Roos BO, Ross S (1988) Theor Chim Acta 73: 155
7. Carter S, Pinnavaia N, Handy NC (1995) Chem Phys Lett 240: 400–408
8. Carter S, Handy NC (1999) J Chem Phys 110: 8417–8423
9. Mussa HY, Tennyson J (1998) J Chem Phys 109: 10885–10892
10. Polyanski OL, Tennyson J (1999) J Chem Phys 110: 5056–5064
11. Åstrand P-O, Karlström G, Engdahl A, Nelander B (1995) J Chem Phys 102: 3534–3554
12. Åstrand P-O, Mikkelsen KV (1996) J Chem Phys 104: 648–653
13. Ruud K, Åstrand P-O, Helgaker T, Mikkelsen KV (1996) J Mol Struct (THEOCHEM) 388: 231–235
14. Åstrand P-O, Ruud K, Mikkelsen KV, Helgaker T (1997) Chem Phys Lett 271: 163–166
15. Åstrand P-O, Ruud K, Mikkelsen KV, Helgaker T (1999) J Chem Phys 110: 9463–9468
16. Truhlar D-G, Garrett BC, Klippenstein SJ (1996) J Phys Chem 100: 12771–12800
17. Bishop DM, Pipin J (1993) J Chem Phys 98: 522–524
18. Kern CW, Matcha RL (1968) J Chem Phys 49: 2081–2091
19. Hylleraas E (1930) Z Phys 65: 209
20. Krohn BJ, Ermler WC, Kern CW (1974) J Chem Phys 60: 22–33
21. Atkins PW (1983) Molecular quantum mechanics, 2nd edn. Oxford University Press, Oxford, second edition
22. Sprandel LL, Kern CW (1972) Mol Phys 24: 1383–1389
23. Buckingham AD (1962) J Chem Phys 36: 3096
24. Buckingham AD, Urland W (1975) Chem Rev 75: 113–117
25. Smith VH Jr, Thakkar AJ, Henneker WH, Liu JW, Liu B, Brown RE (1977) J Chem Phys 67: 3676–3682
26. Helgaker T, Jensen HJ Aa, Jørgensen P, Olsen J, Ruud K, Ågren H, Andersen T, Bak KL, Bakken V, Christiansen O, Dahle P, Dalskov EK, Enevoldsen T, Fernandez B, Heiberg H, Hettema H, Jonsson D, Kirpekar S, Kobayashi R, Koch H, Mikkelsen KV, Norman P, Packer MJ, Saue T, Taylor PR, Vahtras O (1997) DALTON, release 1.0
27. Ruud K, Helgaker T, Bak KL, Jørgensen P, Jensen HJ Aa (1993) J Chem Phys 99: 3847–3859
28. Gauss J, Ruud K, Helgaker T (1996) J Chem Phys 105: 2804
29. Ruud K, Helgaker T, Kobayashi R, Jørgensen P, Bak KL, Jensen HJ Aa (1994) J Chem Phys 100: 8178–8185
30. London F (1937) J Phys Radium 8: 397
31. Pierloot K, Dumez B, Widmark P-O, Roos BO (1995) Theor Chim Acta 90: 87–114
32. The Mathworks Inc (1996) MATLAB version 5, Natict, MA, USA