

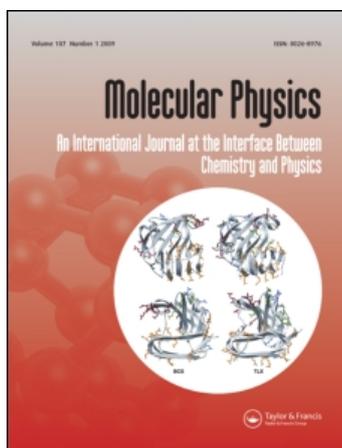
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## INVITED ARTICLE

### Is the adiabatic approximation sufficient to account for the post-Born–Oppenheimer effects on molecular electric dipole moments?

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We estimated the post-Born–Oppenheimer (post-BO) contribution to electric dipole moments by finite-field derivatives of the diagonal Born–Oppenheimer correction computed with correlated electronic wave functions. The new method is used to examine the effect of isotopic substitution on the dipole moments of the HD, LiH, LiD, and H<sub>2</sub><sup>16</sup>O molecules. The non-zero dipole moment of HD is solely due to the post-BO effect and is predicted within a few percent of the best experimental and theoretical results. The post-BO contribution to the dipole moment in LiH and LiD is comparable in magnitude to that in HD, but the difference in total adiabatic dipole moments of LiH and LiD is dominated by the vibrationally averaged BO contribution, and the post-BO contribution is relatively unimportant. However, the post-BO contribution to the dipole moment in H<sub>2</sub>O is *much larger* than the vibrationally averaged BO contribution determined by Lodi *et al.* [J. Chem. Phys. **128**, 044304 (2008)] and is twice as large as the discrepancy between their best theoretical BO estimate and the most recent experimental result. Our findings suggest that for species that are well behaved in the BO sense, the post-BO contribution to molecular electric dipole moments can be described within the adiabatic approximation to a few percent accuracy.

**Keywords:** adiabatic approximation; molecular dipole moments; *ab initio*; electronic structure; Born–Oppenheimer approximation

#### 1. Introduction

In the past quarter-century, several advances in solving the electronic Schrödinger equation have been made. These include the coupled-cluster method [1], the advent of basis-set extrapolation [2] and explicitly correlated techniques [3]; these developments allow electronic energies to be calculated with the accuracy necessary to support experimental observations in fields ranging from high-resolution spectroscopy to thermochemistry. For example, atomisation energies and heats of formation of molecules with a few main-group atoms can be now computed with an astonishing sub-1 kJ mol<sup>-1</sup> accuracy without the use of any adjustable parameters [4–7]. The same fundamental electronic structure technology can be used to construct potential energy surfaces of so-called spectroscopic quality, e.g. the recently constructed *ab initio* adiabatic potential energy surfaces (PESs) of the water isotopologues reproduce all of the measured rovibrational transitions with an average accuracy of better than 1 cm<sup>-1</sup> [8,9]. Empirical adjustment of these

PESs allows reproduction of the same lines with an average accuracy of about 0.02–0.05 cm<sup>-1</sup> [10], approaching the precision of most high-resolution experiments. To achieve such accuracy, it is essential to address issues associated with special relativity as well as deficiencies of the Born–Oppenheimer approximation.

The same fundamental machinery can be used to compute other molecular properties, such as the electric dipole moment, yet such efforts are relatively less established. For example, the first-principles prediction of line intensities in a rovibrational spectrum requires an accurate dipole moment surface (DMS). The electric dipole moment is one of the technically simplest properties to compute in electronic structure theory, but reaching the experimental accuracy is complicated by the need for a high-rank correlated method combined with a large basis set. A recent example is the first-principles DMS of water [11] which was computed with an internally contracted multireference configuration interaction (IC-MRCI) wave function and a large sextuple-zeta

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basis set, with account of scalar relativistic effects. This DMS predicts the line intensities in the rovibrational spectrum of water spectrum, accurate on average to 0.6%. However, the ground-state vibrationally averaged dipole moment predicted by this surface differs from the experimental value of Shostak *et al.* [12,13] by  $\approx 10^{-2}$  D, whereas the cited experimental uncertainty is only  $10^{-4}$  D. Lodi *et al.* improved this agreement to  $\approx 10^{-3}$  D by recomputing the BO dipole moment at the equilibrium geometry using high-level coupled cluster wave functions in combination with basis set extrapolation [11].

One deficiency of the computational approach employed in [11] is the lack of the account for the post-BO effects on the dipole moment. There exists no conclusive evidence for how significant these effects are in general primarily because solving the molecular Schrödinger equation without the help of the BO approximation is extremely costly and is only feasible for very small systems. For example, Adamowicz and co-workers [14–16] have used their variational non-adiabatic approach to compute dipole moments for isotopologues of H<sub>2</sub> and LiH. They found excellent agreement of the computed dipole moments with the experimentally derived dipole moments. However, nonadiabatic computations cannot yet be attempted for general many-electron polyatomics such as H<sub>2</sub>O.

The adiabatic approximation is much simpler computationally and conceptually than the full non-adiabatic treatment because it preserves the idea of a potential energy surface. Thus it should be a reasonable starting point for computing the post-BO effects on molecular properties, such as the dipole moment. This has been recognised previously, e.g. Thorson *et al.* found in 1985 that the post-BO effect on the dipole moment of the HD molecule can be accurately described in the adiabatic picture [17,18]. However, their approach could not be easily generalised to other molecules. Assafrão and Mohallem have recently employed an approximate adiabatic approach to study dipole moments of HD and HDO [19]. Their pseudo-adiabatic approach unfortunately suffers from serious numerical problems, as exhibited by the very strong dependence of the dipole moment function on the basis set [19], and thus reliability of their data is not clearly established.

The objective of this paper is to investigate whether the adiabatic approximation is sufficient to predict quantitatively the post-BO effect on the dipole moment of a simple polyatomic molecule. In Section 2 we will describe our theoretical approach. Results will be discussed in Section 3 and our findings will be summarised in Section 4.

## 2. Theoretical approach

Although the molecular Schrödinger equation is well defined mathematically, its rigorous (nonadiabatic) solution is complicated and, of relevance to us, it does not permit molecules to have a non-zero dipole moment [20]. Specifically, the common definition of the dipole moment is only possible in a molecularly fixed coordinate system, which implies that at least three particles are fixed in a noncollinear arrangement. It is, however, possible to extract a dipole-moment-like quantity from the nonadiabatic computations. Detailed discussion of the costs of avoiding the BO approximation can be found in [20].

The adiabatic approximation employs a product of the BO electronic wave function and a nuclear wave function to represent the eigenfunction of the full molecular Hamiltonian

$$\Psi_{\text{ad}}(\mathbf{r}, \mathbf{R}) = \Psi_{\text{e}}(\mathbf{r}, \mathbf{R})\Psi_{\text{n}}(\mathbf{R}), \quad (1)$$

where  $\mathbf{r}$  is a set of electronic coordinates and  $\mathbf{R}$  is a set of nuclear coordinates. For the sake of simplicity we will put aside the issue of the translational invariance and the undefined norm of the adiabatic wavefunction [21,22]. The expectation value of the molecular Hamiltonian in the presence of a static electric field  $\mathbf{E}$ ,  $\hat{H} = \hat{T}_{\text{e}} + \hat{T}_{\text{n}} + V_{\text{ee}} + V_{\text{ne}} + V_{\text{nn}} - (\hat{\boldsymbol{\mu}}_{\text{e}} + \hat{\boldsymbol{\mu}}_{\text{n}}) \cdot \mathbf{E}$ , in the adiabatic approximation is given by

$$E_{\text{ad}} = \langle \Psi_{\text{ad}} | \hat{H} | \Psi_{\text{ad}} \rangle = \langle \Psi_{\text{n}} | E_{\text{e}} + E_{\text{DBOC}} + \hat{T}_{\text{n}} + V_{\text{nn}} - \hat{\boldsymbol{\mu}}_{\text{n}} \cdot \mathbf{E} | \Psi_{\text{n}} \rangle_{\mathbf{R}}. \quad (2)$$

In Equation (2), we introduced the usual electronic energy in the BO approximation,

$$E_{\text{e}} = \langle \Psi_{\text{e}} | \hat{T}_{\text{e}} + V_{\text{ee}} + V_{\text{ne}} - \hat{\boldsymbol{\mu}}_{\text{e}} \cdot \mathbf{E} | \Psi_{\text{e}} \rangle_{\mathbf{r}}, \quad (3)$$

and the adiabatic correction

$$E_{\text{DBOC}} = \langle \Psi_{\text{e}} | \hat{T}_{\text{n}} | \Psi_{\text{e}} \rangle_{\mathbf{r}}, \quad (4)$$

also known as the diagonal Born–Oppenheimer correction (DBOC) (we will use both terms interchangeably throughout the paper). The bracket subscript in the last three equations denotes the integration variables.

The dipole moment in the adiabatic approximation can be evaluated as the electric field derivative of  $E_{\text{ad}}$  at zero field. This procedure is most straightforward for exact wave functions as well as for approximate wave functions that satisfy the Hellmann–Feynman theorem:

$$\boldsymbol{\mu}_{\text{ad}} = - \left. \frac{dE_{\text{ad}}}{d\mathbf{E}} \right|_{\mathbf{E}=0} = \langle \Psi_{\text{n}} | \boldsymbol{\mu}_{\text{e}} + \boldsymbol{\mu}_{\text{DBOC}} + \hat{\boldsymbol{\mu}}_{\text{n}} | \Psi_{\text{n}} \rangle_{\mathbf{R}} \quad (5)$$

where the electronic and DBOC dipole moments are:

$$\boldsymbol{\mu}_e = \langle \Psi_e | \hat{\boldsymbol{\mu}}_e | \Psi_e \rangle_{\mathbf{r}}, \quad (6)$$

$$\boldsymbol{\mu}_{\text{DBOC}} = - \left. \frac{dE_{\text{DBOC}}}{d\mathbf{E}} \right|_{E=0}. \quad (7)$$

Note that the latter term occurs only due to the implicit dependence of the electronic wave function on the electric field and cannot be expressed as a simple expectation value. Once again [20], a non-zero dipole moment can only be obtained if the rotational component of  $\Psi_n$  is eliminated. Thus, the dipole moment in the adiabatic approximation is a sum of the vibrationally averaged BO dipole moment and the vibrationally averaged DBOC contribution:

$$\begin{aligned} \boldsymbol{\mu}_{\text{ad}} &= \langle \Psi_n | \boldsymbol{\mu}_e + \hat{\boldsymbol{\mu}}_n | \Psi_n \rangle_{\mathbf{R}_v} + \langle \Psi_n | \boldsymbol{\mu}_{\text{DBOC}} | \Psi_n \rangle_{\mathbf{R}_v} \\ &\equiv \langle \boldsymbol{\mu}_{\text{BO}} \rangle + \langle \boldsymbol{\mu}_{\text{DBOC}} \rangle, \end{aligned} \quad (8)$$

where subscript  $\mathbf{R}_v$  denotes integration over vibrational coordinates only. Note that both terms in Equation (8) depend on nuclear masses indirectly, through the vibrational wave function, whereas  $\langle \boldsymbol{\mu}_{\text{DBOC}} \rangle$  also includes such dependence through the  $\boldsymbol{\mu}_{\text{DBOC}}$  quantity. The latter is a purely post-BO contribution to the dipole moment and is the focus of this work.

In this study, we computed  $\boldsymbol{\mu}_{\text{DBOC}}$  by differentiating  $E_{\text{DBOC}}$  via finite differences of the electric field. To attain high accuracy we evaluated  $E_{\text{DBOC}}$  with correlated electronic wave functions. Recently several groups devised general methods for computing the adiabatic energy correction at correlated levels of theory using finite-difference [23,24] and analytic [25,26] techniques. In this work we use the procedure for evaluating  $E_{\text{DBOC}}$  with Hartree–Fock and configuration interaction wave functions by finite differences of nuclear positions previously described by one of us [24]. The adiabatic correction is evaluated using the so-called Born–Handy ansatz [22] first introduced in this form by Handy *et al.* [27]:

$$\begin{aligned} E_{\text{DBOC}} &= \sum_I^{N_{\text{coor}}} \langle \Psi_e | - \frac{1}{2M_I} \nabla_I^2 | \Psi_e \rangle \\ &= \sum_I^{N_{\text{coor}}} \frac{1}{2M_I} \left\langle \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \middle| \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \right\rangle, \end{aligned} \quad (9)$$

where the sum is over the nuclear *Cartesian* coordinates. The nuclear derivatives of the electronic wave function are easily computed by the technique of central differences. Whereas the approach of [24] utilised a two-point formula, here, we rely on the

following more accurate and numerically stable four-point formula:

$$\frac{\partial \Psi_e}{\partial \mathbf{R}_I} = \frac{-\Psi_e^{+2\delta} + 8\Psi_e^{+\delta} - 8\Psi_e^{-\delta} + \Psi_e^{-2\delta}}{12\delta}, \quad (10)$$

in which the superscripts denote the corresponding displacement of  $\mathbf{R}_I$ . The finite-difference approximation to Equation (9) then involves overlaps of wave functions computed at displaced geometries, which, in our approach, are computed using a simple string-based approach [24]. Because our goal is to obtain the field-derivative of  $E_{\text{DBOC}}$ , all electronic wave functions were computed without the use of the point-group symmetry, although our finite-difference DBOC procedure can utilise the point-group symmetry whenever possible.

All computations were performed with a developmental version of the PSI package [28]. Dunning’s correlation-consistent basis sets were used for all electronic wave function expansions [29–31]. The following conversion factors have been employed:  $m_e = 5.485799110 \times 10^{-4}$  u,  $1 \text{ D} = 2.54175$  au. Nuclear masses used to evaluate DBOC were derived from the atomic masses [32] by subtracting the mass of the electrons.<sup>1</sup> Atomic masses were used in solving the nuclear Schrödinger equation. DBOC computations on H<sub>2</sub>O utilised frozen-core CISD wave functions to reduce the computational effort. The effect of the frozen-core approximation on the adiabatic dipole moment contribution was estimated at ~5% for LiH at the aug-cc-pCVTZ CISD level.

### 3. Results

#### 3.1. The hydrogen molecule

The existence of a small dipole moment in the heteroisotopologues of H<sub>2</sub> has been postulated as early as 1935 by Wick [33] and subsequently studied computationally and experimentally (see Table 1). Its origin is routinely, but imprecisely, attributed to ‘nonadiabatic’ effects [35,36]. Indeed, it appears to be due to the coupling of the electronic and nuclear motions, but even within the adiabatic picture the heteroisotopologues have non-zero dipole moments due to a non-zero  $\boldsymbol{\mu}_{\text{DBOC}}$  term in Equation (8). Thorson *et al.* [17,18] apparently were the first to recognise this. They used essentially adiabatic arguments, i.e. that the occurrence of the dipole moment is due to the difference in the electronic reduced mass near different isotopes, to evaluate the dipole moment function. At the equilibrium internuclear distance their dipole moment function was in very good agreement with earlier nonadiabatic results. Recently, Assafrão

Table 1. The electric dipole moment for the HD molecule.

Method	Source	$\mu$ , $10^{-4}$ D
Perturbative nonadiabatic	[34]	8.36
Perturbative nonadiabatic	[35]	8.31
Variational nonadiabatic	[15]	8.31
$\langle\mu_{\text{ad}}\rangle$	This work	8.68
Experiment	[36]	8.78

and Mohallem [19] pursued another approximate adiabatic approach, with similar results. In contrast to these ‘pseudoadiabatic’ efforts, here we compute the dipole moment using the rigorous adiabatic framework of Equation (8).

To determine how sensitive  $\mu_{\text{DBOC}}$  is to the quality of the electronic wave function, we computed it using several levels of theory with the internuclear distance fixed at  $R=1.4a_0$  (see Table 2). The basis set dependence of the correction evaluated at the Hartree–Fock level is negligible, however the lack of electron correlation introduces roughly a 10% error. The DBOC correction at the FCI level is essentially converged with respect to the basis set size at the triple-zeta level. The most accurate estimate, at the FCI/aug-cc-pV5Z level, agrees very well with the nonadiabatic result of Ford and Browne ( $8.371 \times 10^{-4}$  D) [35] and agrees almost exactly with the result of Thorson *et al.* obtained with a pseudoadiabatic approach ( $8.51 \times 10^{-4}$  D) [17,18]. The latter agreement is remarkable, especially considering that our approach is technically rather different from that of Thorson *et al.*

We subsequently evaluated the vibrationally averaged FCI/aug-cc-pVQZ DBOC contribution,  $\langle\mu_{\text{DBOC}}\rangle$ , by numerical integration. The ground-state vibrational wavefunction of HD was determined by the Cooley–Numerov method. Since the DBOC energy is rather small, we approximated the potential energy in the nuclear Schrödinger equation by the BO potential,  $E_e + V_{\text{nn}}$ , evaluated at the FCI/aug-cc-pVQZ level. The resulting value,  $8.68 \times 10^{-4}$  D, agrees excellently with the experimental value of  $8.78 \times 10^{-4}$  D by Nelson and Tabisz [36]. A more reliable estimate is provided by the three accurate nonadiabatic theoretical predictions (see Table 1), which mutually agree within  $5 \times 10^{-6}$  D; the experimental value differs from these theoretical results by  $\sim 0.5 \times 10^{-4}$  D. Our adiabatic result is within  $\approx 4\%$  of the average of the three nonadiabatic results. This discrepancy should probably be attributed to the remaining post-adiabatic effects. Nevertheless, the 4% accuracy of the simple adiabatic contribution is satisfactory for practical purposes.

Table 2. Variation of the DBOC component of the dipole moment of the HD molecule (in  $10^{-4}$  D) with respect to the basis set size and the wave function type.

Basis	Hartree–Fock	FCI
aug-cc-pVDZ	7.68	8.74
aug-cc-pVTZ	7.64	8.48
aug-cc-pVQZ	7.68	8.50
aug-cc-pV5Z	7.68	8.52

The internuclear distance is fixed at  $R=1.4a_0$ . Ford and Browne’s perturbation theoretical estimate of the dipole moment at this geometry  $8.371 \times 10^{-4}$  D [35].

### 3.2. Lithium hydride

LiH and its isotopologues have a non-zero BO dipole moment and thus the post-BO dipole moment contribution can be assumed to be relatively minor. Cafiero and Adamowicz computed the dipole moments of LiH and LiD using the variational nonadiabatic approach [14] and obtained values in perfect agreement with the experimental values (see Table 3). Note that the substitution of H by D reduces the magnitude of the dipole moment by  $\approx 0.014$  D. This isotopic effect on the dipole moment is much larger than the difference between the dipole moments of  $\text{H}_2$  and HD and clearly cannot be explained by the post-BO contribution alone.

To obtain  $\langle\mu_{\text{BO}}\rangle$  for LiH and LiD, we followed a computational protocol similar to that for HD. The BO potential energy surface and dipole moments were evaluated at the CCSD(T)/aug-cc-pCVQZ level of theory whereas the DBOC dipole moment was computed with the all-electron CISD/aug-cc-pVTZ electronic wave function. Table 3 presents the computed values. The agreement between the computed  $\langle\mu_{\text{ad}}\rangle$  and the nonadiabatic theoretical as well as the experimental results is relatively poor. The discrepancy is likely due to the error of the BO value. Unfortunately, much more expensive electronic structure computations will be necessary to pinpoint the uncertainty in the BO dipole moment to that of the experimental value even for such a small system.

We also examined the isotopic effect in more detail, i.e. the difference in the dipole moments of LiH and LiD. This quantity should be less sensitive to the quality of the electronic wave function because of significant cancellation of errors. The bulk of the isotopic effect on the dipole moment, 0.0135 D, is due to the nuclear mass dependence of  $\langle\mu_{\text{BO}}\rangle$  via the vibrational wave function. By comparison, the contribution of  $\langle\mu_{\text{DBOC}}\rangle$  to the total dipole moments and to the isotopic effect is much smaller, at only  $-0.0006$  D.

Table 3. Electric dipole moments (in D) of LiH and LiD and their difference,  $\delta$ .

Method	Source	LiH	LiD	$\delta$
$\langle\mu_{\text{BO}}\rangle$	This work	5.8882	5.8747	0.0135
$\langle\mu_{\text{DBOC}}\rangle$	This work	-0.0006	0.0000	-0.0006
$\langle\mu_{\text{ad}}\rangle$	This work	5.8876	5.8747	0.0129
Variational nonadiabatic	[14]	5.8816	5.8684	0.0132
Experiment	[37]	$5.882 \pm 0.003$	$5.868 \pm 0.003$	0.014

The adiabatic value for the isotopic effect is within 0.0003 D of the value predicted by the nonadiabatic approach of Cafiero and Adamowicz [14]. Thus, although the DBOC dipole moment is small for LiH and LiD, it cannot be neglected to reach better than  $10^{-3}$  D accuracy.

### 3.3. The water molecule

The water molecule occupies a special place in molecular quantum mechanics, as its electronic structure is probably the most intensely studied of any triatomic molecule. Unfortunately, fully nonadiabatic computations on a water molecule are presently not possible. Thus all existing studies of the dipole moment of water assume the BO approximation.

The most extensive examination of the dipole moment surface of water to date is by Lodi *et al.* [11]. The authors computed their dipole moment surface, referred to as ‘CVR’, using a valence internally contracted multireference CI wave function with a large aug-cc-pV6Z basis, and included an additive core and scalar relativistic corrections. Nevertheless, such an elaborate approach turned out to be sufficient only to compute the vibrationally averaged dipole moment to an accuracy of  $\approx 10^{-2}$  D (see Tables VIII and IX in [11]). By comparison, the most recent experimental value, from Shostak *et al.* [12,13], is accurate to  $\approx 10^{-4}$  D. In an attempt to match the accuracy of the experimental number, Lodi *et al.* obtained the best estimate of the dipole moment from the nonrelativistic BO dipole moment computed at the equilibrium geometry [38] using a series of high-level coupled-cluster wave functions and basis set extrapolation. To this best nonrelativistic BO value of 1.8580 D, they added a scalar relativistic correction (-0.0043 D) and the effect of vibrational averaging (0.0003 D) computed using their new CVR DMS. The total estimate of the dipole moment,  $1.8540 \pm 0.0015$  D, is within the error bars of the experimental value of Shostak *et al.* (see Table 4).

To estimate the post-BO contribution to the best dipole moment value of Lodi *et al.*, we evaluated the

Table 4. Electric dipole moments (in D) of  $\text{H}_2^{16}\text{O}$ .

Method	Source	$\text{H}_2^{16}\text{O}$
$\langle\mu_{\text{BO}}\rangle$	[11]	$1.8540 \pm 0.0015$
$\mu_{\text{DBOC}}$	This work	0.0020
$\langle\mu_{\text{ad}}\rangle$	This work	$1.8560 \pm 0.0015$
Experiment	[12]	$1.85498 \pm 0.00009$

DBOC dipole moment,  $\mu_{\text{DBOC}}$ , of  $\text{H}_2\text{O}$  at the best estimate of the equilibrium geometry ( $r=0.95782$  Å and  $\theta=104.485^\circ$ ) [38] using the frozen-core CISD/aug-cc-pVTZ electronic wave function. Somewhat unexpectedly, the computed DBOC value (0.0020 D) is significantly greater in magnitude than the effect of vibrational averaging and is almost half as large as the relativistic contribution. Adding the DBOC value to the best  $\langle\mu_{\text{BO}}\rangle$  value of Lodi *et al.*, we obtained 1.8560 D, our best estimate of the adiabatic dipole moment. Thus inclusion of the post-BO contribution changes the sign of the discrepancy with respect to the experimental result but fails to reduce its magnitude.

At this point we can only speculate about the remaining sources of the discrepancy between the theoretical and experimental values. (1) The magnitude of the post-adiabatic contribution to the dipole moment is unknown. Based on our data for HD, these effects are unlikely to be greater than a few percent of  $\mu_{\text{DBOC}}$  near the equilibrium geometry, and thus doubtful to be the source of the discrepancy. (2) The BO contribution to the dipole moment as computed by Lodi *et al.* still has a very large uncertainty. This uncertainty can perhaps be reduced by the use of explicitly correlated coupled-cluster R12 methods [39,40]. (3) It may also be necessary to revisit the force-field and DMS parameters used by Shostak *et al.* to interpret their data. Furthermore, it may be more meaningful to avoid computing the dipole moment, which cannot be determined directly from the experiment, and instead concentrate on prediction of the intensities of selected lines in molecular Stark spectra.

In conclusion, our data unequivocally demonstrated for the first time the importance of the post-BO effects to the spectroscopically accurate determination of the dipole moment of water. Further work is necessary to determine the vibrational average of this contribution for the most important water isotopologues.

#### 4. Summary and conclusions

In this work, we computed the electric dipole moments for several simple molecules within the adiabatic approximation. The post-BO contribution in the adiabatic picture comes from the field derivative of the DBOC, which in our approach was computed by finite differences. We showed that the dipole moment of HD in the adiabatic approximation can be accurately predicted to a few percent compared to the more rigorous nonadiabatic predictions. The common statement in literature that the non-zero dipole moment in HD occurs due to nonadiabatic effects is incorrect and provides a perhaps misleading view of the magnitude of true nonadiabatic effects in HD.

We also found that the effect of isotopic substitution on the dipole moment in the LiH/LiD pair is dominated by the mass dependence of the BO contribution averaged over the vibrational wave function. The DBOC increment to the dipole moment in this case is similar to the magnitude of the dipole moment in HD.

Our investigation of the post-BO effect of the water molecule indicated that the DBOC effect on the dipole moment is much larger than the effect of vibrational averaging of the BO value and is comparable in magnitude to the relativistic effect on the dipole moment [11]. The DBOC effect is twice as large as the discrepancy between the best experimental and computed BO estimates of the dipole moment. Re-examination of the sources of error in these values is, in our opinion, warranted.

Our findings suggest that the post-BO contribution to molecular electric dipole moments must be included to compute highly accurate dipole moments. Recent progress in the evaluation of the DBOC correction using correlated electronic wave functions has made it relatively straightforward to evaluate such contributions. For HD, the adiabatic approximation can predict the dipole moment accurately to a few percent. This suggests that for more complex species that are well behaved in the BO sense, the post-BO dipole moment can be reliably computed within the adiabatic approximation.

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#### Note

1. This procedure neglects the relativistic correction to the mass, but for all cases considered here such a correction is on the order of  $10^{-6}u$  and therefore can be safely neglected.

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