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functions of the diagonal Born-Oppenheimer correction for the $X^2\Pi$ and $A^2\Sigma^+$ states of the hydroxyl (OH) radical

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A high-precision non-empirical calculation of the diagonal Born–Oppenheimer correction (DBOC) to the mass-invariant Born–Oppenheimer potential energy curves of the ground $X^2\Pi$ and excited $A^2\Sigma^+$ states of the diatomic OH radical is reported. The *ab initio* calculations were performed using the single-reference coupled-cluster (CC) approach over a wide range of internuclear distances. We investigated the dependence of the DBOC curve on the number of cluster amplitudes included in the treatment (up to CCSDTQ) and on the completeness of the basis set. We found a strong sensitivity of the DBOC correction to the basis set size and the number of excitations accounted for. Numerical agreement of the DBOC values at the dissociation limit with the mass shift of the corresponding isolated atoms is demonstrated. The obtained *ab initio* DBOC functions enable a simultaneous treatment of all OH isotopologues within a single adiabatic (and/or nonadiabatic) model founded on a mass-invariant set of electronic structure parameters that possess clear physical meaning.

Keywords: OH radical, diagonal Born–Oppenheimer correction, non-empirical calculations, electronic structure of molecules.

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1. Introduction

The interest in studying the free radical hydroxyl (OH) is largely because this molecule is widespread in the Universe. I.S. Shklovsky already in the last mid century suggested that lines of interstellar molecules, including OH molecules, can be found in the radio emission of Galaxy [1,2]. Indeed, hydroxyl turned out to be one of the first astronomical molecules detected using radio spectroscopic observations. Radio frequency absorption lines of the OH radical were detected for the first time in the spectrum of Cassiopeia A constellation in 1963 [3]. OH spectral lines serve as a reliable tool for determining the oxygen content in the atmosphere of the Sun and other stars [4–6]. Using the spectrum of OH molecule, it is possible to observe the expansion of shells of evolved stars, star formation regions, and supernova remnants [7,8]. The night glow in the Earth's atmosphere is caused by the Meinel bands [9–11] — optical transitions between the vibrantly rotating levels of the ground electronic state of $X^2\Pi$ hydroxyl. Being a strong oxidizer, the OH molecule impacts the lifetime of carbon monoxide, methane and other volatile organic substances in the Earth's atmosphere [12,13]. The OH radical has also been detected in the atmosphere of Venus [14], Mars [15] and even WASP-33b exoplanet [16].

There's a slew of literature on OH spectroscopy. Here we will briefly summarize only some of the most important articles related to the problems described herein, in no way pretending to be an exhaustive literary review. The spectroscopic data of the ground and low-lying excited states of the OH molecule was analyzed in a large number of studies using both experimental and semi-empirical methods [11,17–30], and using *ab initio* quantum chemical calculations [28,30–41]. Empirical and non-empirical potential energy curves (PEC) of the ground, $X^2\Pi$, and excited $A^2\Sigma^+$, states of OH radical which form an electronic system $A^2\Sigma^+ - X^2\Pi$ were obtained in the studies [11,25,28–30,32,33,36,38,40,41]. One of the first publications where the results of ab initio analysis of PEC for the hydroxyl molecule were presented were the studies [32,33]. To obtain potential curves in jcite32, the method of optimized valence configurations was used. In jcite33, the method of configuration interaction (CI) using natural orbitals and the method of coupled electron pairs were used. In the majority of studies jcite28,30,36-41 to account for dynamic correlation in the construction of PEC, the method of multi-link configuration interaction with single and double excitations (MR-CISD) was chosen.

Unfortunately, the presented ab initio PEC calculations from previous years are all have one common drawback — they were all made exclusively within Born-Oppenheimer approximation, i.e. they neglected the presence of a mass-dependent part associated with the so-called diagonal Born-Oppenheimer correction (DBOC) [42–44], which in the molecular coordinate system is inversely proportional to the reduced mass of the molecule μ. Taking into account the very small value μ for the hydroxyl molecule, DBOC is not expected to be negligibly small for all known OH isotopologues, therefore, in order to improve the agreement between quantum chemical calculations and spectral experiment, it would be necessary to take into account the presence of an adiabatic correction, which is the leading correction to the standard BO potential. One of the main features of DBOC is that when it is added to the mass-invariant BO potential this does not actually affect the adiabatic character of the molecular system concept as a whole, but only clarifies the specific form of PEC of the isolated electronic state for each isotopologue of the molecule.

The ab initio DBOC analysis is also critical for the successful solution of the inverse spectroscopic problem — semi-empirical construction (restoration) of the effective interatomic molecule potential based on precision experimental data on its spectrum energy structure (measured position of spectral lines). Indeed, when processing experimental data of only one isotopologue, it is impossible to separate the mass-invariant (BO) and mass-dependent (DBOC) parts in the empiric PEC, and thus build and use a single PEC for all isotopologues. Knowing *a priori* DBOC as an explicit function of the reduced mass of a molecule makes this task much easier.

In this study the method of single-link coupled clusters (CC) was used *ab initio* to calculate the diagonal adiabatic correction (DBOC) to BO-curves of potential energy of the ground state, $X^2\Pi$, and low-lying excited state $A^2\Sigma^+$, of OH molecule in a wide range of internuclear distances, and the dependence of DBOC on the number of accounted electron excitations and the degree of completeness of the basis set was also analyzed.

2. Quantum chemical calculation method

The diagonal adiabatic correction was introduced by M. Born and K. Huang [46] and is defined as

$$\Delta E_{\mathrm{DBOC}}(\mathbf{R}) = \langle \Psi(\mathbf{r};\mathbf{R}) \mid \hat{T}_{\mathrm{N}}(\mathbf{R}) \mid \Psi(\mathbf{r};\mathbf{R}) \rangle, \qquad (1)$$

where Ψ is the normalized electron wave function obtained within BO approximation, and $\hat{T}_{\mathrm{N}}$ is the kinetic energy operator of the nuclei. The integration in the equation is carried out for all electronic coordinates $\mathbf{r}$. Formula (1) was theoretically justified in [42]. It is not difficult to obtain an alternative formula, which is often used for calculations:

$$\Delta E_{\mathrm{DBOC}}(\mathbf{R}) = \sum_A \frac{\hbar^2}{2M_A} \langle \nabla_A \Psi(\mathbf{r};\mathbf{R}) | \nabla_A \Psi(\mathbf{r};\mathbf{R}) \rangle,$$

where M_A — mass of the nucleus A. Thus, calculating the average nuclei kinetic energy operator allows to take into account the molecule electronic energy versus the mass of its atoms as an addition to the mass-invariant BO potential.

Usually, the finite difference method is used to estimate ΔE_{DBOC}, however, corrections at the level of Hartree-Fock approximation (HF) may be calculated by analytically differentiating the corresponding electronic wave functions [47,48]. To obtain a high-accuracy DBOC correction, it is already needed to allow for the correlation effects, that is, the use of methods such as the configuration interaction method (CI) or the coupled cluster method (CC). Formulae for calculating the DBOC at CI and CC levels were derived in [44,49].

To account for the effects of electronic correlation, we used the single-link coupled cluster (CC) method. The shape of DBOC curve was studied as a function of the number of cluster amplitudes, in particular, calculations were performed taking into account only single and double excitations (CCSD), triple (CCSDT) and quadruple cluster amplitudes (CCSDTQ). The standard correlation-oriented basis set of primitive Gaussian functions cc-pVnZ with cardinal number n = D, T, Q [50] was taken as the basis set. Additionally, the contribution of diffuse functions was investigated using calculations based on aug-cc-pVTZ [51]. At the same time, the correlation 7 of electrons was taken into account, which, together with all virtual orbitals, were included in the active space. The molecular orbitals were constructed by HF method using cfour software package [52]. The necessary transformation of integrals was also performed in this software package. Calculations using the linked cluster method were performed using program mrcc [53,54].

3. Calculation results

Figure 1 shows the curves of the adiabatic correction to the potential energy of the ground state $X^2\Pi$ of OH molecule obtained by CCSD, CCSDT, and CCSDTQ methods. You can see that on the curve obtained by CCSD method, a „hump" appears in the region 1.9 Å the height of which is about 20 cm^{-1}. When three-fold excitations are taken into account, the hump decreases to about 7 cm^{-1}, however, at large distances, the DBOC value starts rising again. The inclusion of fourfold cluster amplitudes in the calculation solves this problem.

Figure 2 illustrates the ground state $X^2\Pi$ DBOC of OH radical versus internuclear distance, calculated in various basis sets using CCSDTQ method. Larger basis set leads both to an increase in the well depth, that is, the difference between the minimum of DBOC curve and DBOC value over long distances, and to a higher hump, which is clearly demonstrated in Tables 1 and 2, respectively. The change in DBOC depending on the basis set used during transition from cc-pVTZ basis to cc-pVQZ basis is less than during transition from cc-pVDZ to cc-pVTZ, which indicates convergence over the basis set. The diffuse functions added to cc-pVTZ basis also increase the well depth and hump height. Larger set of the basis functions impacts the DBOC on short distances in a much less extent

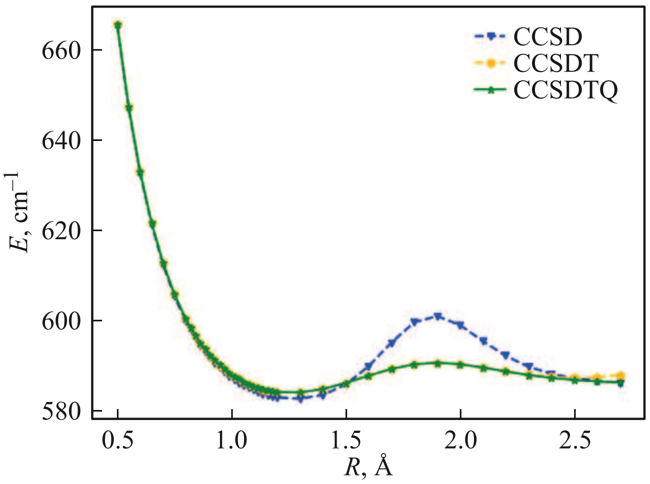

Figure 1. DBOC correction to the potential energy of the ground state $X^2\Pi$ of the hydroxyl molecule as a function of the internuclear distance calculated by CCSD, CCSDT and CCSDTQ methods in cc-pVDZ basis.

Table 1. Well depth (in cm^{-1}) of DBOC function for the ground state $X^2\Pi$ of hydroxyl molecule versus the basis set used, as obtained by CCSDTQ method

Basis	Well depth
cc-pVDZ	2.3
cc-pVTZ	7.3
cc-pVQZ	9.1
aug-cc-pVTZ	9.6

Table 2. The hump height (in cm^{-1}) of DBOC function for the ground state $X^2\Pi$ of hydroxyl molecule versus the number of electronic excitations taken into account and the basis set used

Basis	CCSDT	CCSDTQ
cc-pVDZ	6.3	6.3
cc-pVTZ	10.3	10.1
aug-cc-pVTZ	11.3	11.0
cc-pVQZ	11.4	11.1
aug-cc-pVQZ	11.6	

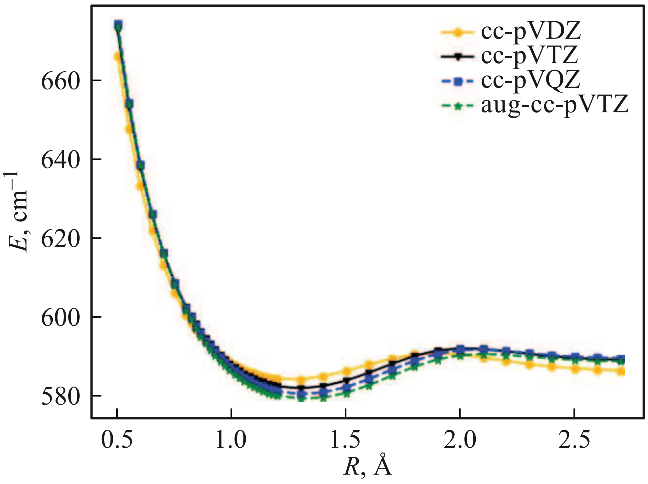

Figure 2. DBOC correction to the potential energy of the ground state $X^2\Pi$ of hydroxyl molecule as a function of internuclear distance calculated by CCSDTQ in cc-pVnZ (n = D, T, Q) and aug-cc-pVTZ basis.

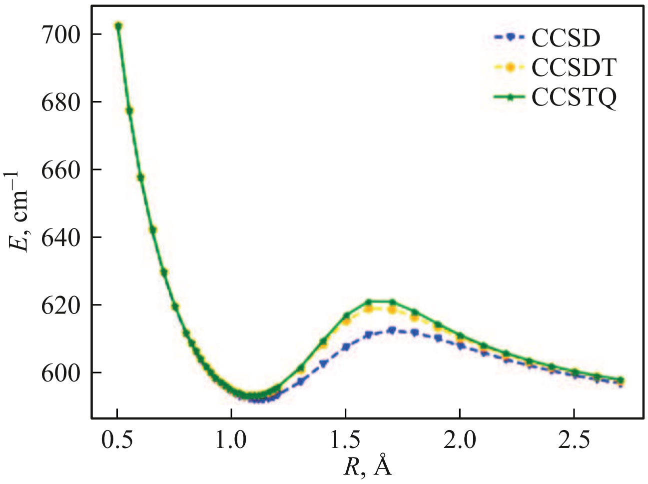

Figure 3. DBOC correction to the potential energy of the excited state $A^2\Sigma^+$ of hydroxyl molecule as a function of the internuclear distance found by CCSD, CCSDT and CCSDTQ methods in cc-pVDZ basis.

compared to the longer distances, therefore, convergence with respect to the basis set is reached faster for the hump height than for the well depth. The calculation of DBOC correction using CCSDTQ method and aug-cc-pVQZ basis set is labor-intensive, therefore, we used CCSDT method to approximate the contribution of diffuse functions added to cc-pVQZ basis set to the height of the hump. The CCSDT method at short distances reproduces well the results obtained using CCSDTQ method, as can be seen in Fig. 1. Adding diffuse functions to c-pVQZ basis set increases the hump height much less than adding diffuse functions to the cc-pVTZ basis set. The curve obtained using aug-cc-pVTZ basis is considered the final DBOC curve.

The curves of the adiabatic correction to the potential energy of the first excited state $A^2\Sigma^+$ of OH molecule found by the coupled cluster method with a different number of cluster amplitudes are shown in Fig. 3. As can be seen, unlike the ground state, with a higher number of excitations included in the calculation, the hump on DBOC curve grows rather than declines. There is a convergence of the calculation results from the number of excitations taken into account: when adding fourfold cluster amplitudes to the calculation, the hump size increases noticeably less than when adding three-fold amplitudes.

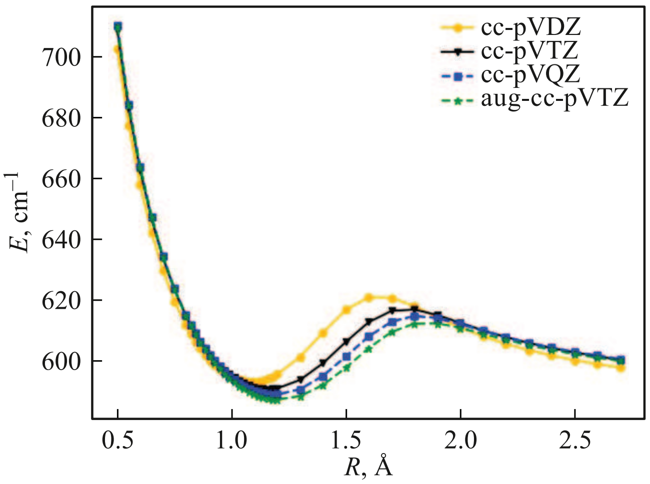

Figure 4. DBOC correction to the potential energy of the excited state $A^2\Sigma^+$ of hydroxyl molecule as a function of internuclear distance calculated by CCSDTQ in cc-pVnZ (n = D, T, Q) and aug-cc-pVTZ basis.

For the final analysis of DBOC curve of the excited state $A^2\Sigma^+$ of OH molecule, we used aug-cc-pVTZ basis. DBOC of the first excited state $A^2\Sigma^+$ of OH radical versus internuclear distance calculated in the basis sets cc-pVnZ (n = D, T, Q) and aug-cc-pVTZ within CCSDTQ method, is shown in Fig. 4. The hump declines slightly from 28 to 25 cm^{-1} as the basis set grows, while the minimum of the curve and the hump noticeably shift to the right.

DBOC correction for a molecule at the dissociation limit should tend to a mass shift (MS) of isolated atoms. The non-relativistic theory of a mass shift was first formulated in [55]. The mass shift can be represented as the sum of the normal mass shift (NMS) and the specific mass shift (SMS). NMS is single-particle operator and is defined as

$$H_{\text{NMS}} = \frac{1}{2M_A}\sum_i \mathbf{p}_i^2, \tag{3}$$

where $\mathbf{p}_i$ — momentum operator. The two-part SMS operator can be written as

$$H_{\text{SMS}} = \frac{1}{2M_A}\sum_{i\neq j} \mathbf{p}_i \cdot \mathbf{p}_j. \tag{4}$$

The maximum value of DBOC for a molecule at the dissociation limit can be estimated by calculating DBOC for isolated atoms. Table 2 gives the values of DBOC, NMS, SMS and MS for the ground state, ^{3}P, and excited state, ^{1}D, of the oxygen atom, as well as for the ground ^2S-state of the hydrogen atom. DBOC and NMS were calculated in aug-cc-pVTZ basis using CCSDTQ method for oxygen and HF method for hydrogen. NMS is found as

$$E_{\text{NMS}} = -E\frac{m_{\text{e}}}{M_A}, \tag{5}$$

where E — full atom energy as calculated, and m_{e} – mass of the electron. The SMS value for the oxygen atom was taken from [56]. From Table 3 it can be seen that the values of DBOC and MS for atoms are close. A slight difference between DBOC and MS of the ground state ^3P of oxygen atom is due to the fact that in [56] the CI method was used to calculate SMS, and DBOC in our work was found using CC method, as well as the fact that various calculations were used as basis sets.

Table 3. The values of DBOC, NMS, SMS, and MS (in cm^{-1}) for the ground state ^{3}P, and excited state ^{1}D of oxygen atom and the ground state ^2S of hydrogen atom

Atom	DBOC	NMS	SMS	MS
O(^{3}P)	526.2	564.2	−29.2	535.0
O(^{1}D)	526.0	563.7		
H(^{2}S)	59.7	59.7	0	59.7

The ground state $X^2\Pi$ of OH molecule implies the atomic limit $O(^3P) + H(^2S)$, and the excited state $A^2\Sigma^+$ – $O(^1D) + H(^2S)$. Knowing the amount of DBOC for atoms and DBOC for the equilibrium configuration of molecule, it is possible to determine the contribution of DBOC to the dissociation energy. For the basic, $X^2\Pi$, and excited $A^2\Sigma^+$ hydroxyl states, this contribution is 1.5 cm^{-1}, which coincides in order of magnitude with the contribution from quantum electrodynamic effects in [41].

4. Conclusion

In this paper, for the first time, an ab initio analysis of DBOC correction to BO potential energy of the ground $X^2\Pi$, and the first excited $A^2\Sigma^+$ states of the OH molecule was made. The dependence of the adiabatic correction curve on the number of excitations included in the analysis and the basis set is investigated. The results obtained indicate that it is crucial to take into account excitations of higher orders and a larger number of basic functions to provide a precise delineation of DBOC function. The final curves of DBOC versus internuclear distance were obtained using CCSDTQ method and the aug-cc-pVTZ basis. A good agreement between the values of DBOC at the dissociation limit and MS for isolated atoms has been demonstrated.

We hope that using the *ab initio* DBOC functions to build effective interatomic potentials will make the delineation of the energy and radiation characteristics of $X^2\Pi$ and $A^2\Sigma^+$ states of hydroxyl molecule more reliable which can be achieved by considering all of its isotopologues within a single spectroscopic model with a mass-independent set of electronic structural parameters having a clear physical meaning.

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Conflict of interest

The authors declare that they have no conflict of interest.

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