Supporting Information: "Anomalous description of anharmonicity of bending motions of carbon-carbon double bonded molecules with the MP2 method: Ethylene as a case study"

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I. THE VIBRATIONAL SELF-CONSISTENT FIELD (VSCF) THEORY

The vibrational self-consistent field theory[1–6] is one of the most used methodology to compute anharmonic vibrational spectra of polyatomic molecules. The VSCF invokes single particle approximation for the vibrational many-body problem. Here, the vibrational wave-function of a N mode system is written as a product of N one mode functions

$$\Phi_{q_1,q_2,....,q_N} = \Pi_i \phi_{n_i}^i(q_i). \tag{1}$$

Each of such one mode function, usually refereed as modals, are expanded in an orthonormal basis functions (usually harmonic oscillator basis)

$$\phi_{n_i}^i = \sum_m \chi_m^i C_{mn}. \tag{2}$$

The modals are then variationally optimized by minimizing the expectation values of vibrational Hamiltonian with respect to these basis functions. This leads to the working equations for the optimized modals

$$(h_{eff}^i - \epsilon_n^{(i)})\phi_{n_i}^i(q_i) = 0. \tag{3}$$

Here h_{eff}^i is the effective one-body Hamiltonian for the ith mode whose potential is generated by averaging the non-separable many-body Hamiltonian over other modes. The Eq. 3 are solved in self-consistent manner. Once the optimized modals are obtained, the VSCF energy of a particular vibrational state is obtained as the expectation value of the vibrational Hamiltonian with the optimized wavefunctions for that state.

II. THE VIBRATIONAL COUPLED CLUSTER METHOD

There are two different representations possible to formulate the vibrational coupled cluster method. One is the basis set representation, formulated and used extensively by Christiansen and co-workers[5, 7, 8]. The second one is the bosonic representation developed and used by Prasad and co-workers[9–11]. We used bosonic representation in this study.

In the formulation of the VCCM in bosonic representation, first the effective harmonic oscillator (EHO) approximation[6, 9, 10] is invoked to get optimized reference function for

the vibrational ground-state. In the EHO approximation, a product of N Gaussian functions

$$\Phi_0 = exp(-\sum_i \omega_i(q_i - q_i^0)^2/2), \tag{4}$$

and is variationally optimized with respect to the ω_i and q_i^0 to obtain the vibrational ground-state wavefunction for a molecule with N vibrational modes. The harmonic oscillator ladder operators are then defined with respect to this optimized Φ_0

$$a_i = \sqrt{\frac{\omega_i}{2}}(q_i - q_i^0 + \frac{1}{\omega_i}\frac{q}{dq_i}) \tag{5}$$

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2}}(q_i - q_i^0 - \frac{1}{\omega_i}\frac{q}{dq_i}) \tag{6}$$

We note that the optimized reference function Φ_0 is the vacuum state for a_i.

Next, the VCCM wavefunction is parametrized with a double-exponential wave operator operating on the optimized vacuum state Φ_0,

$$|\Psi_g\rangle = e^{-S}e^\sigma|\Phi_0\rangle. \tag{7}$$

The cluster operators S and σ are expanded as

$$S = \sum_i s_i a_i^\dagger + \sum_{i\leq j} s_{ij} a_i^\dagger a_j^\dagger + \sum_{i\leq j\leq k} s_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger + \ldots \tag{8}$$

$$\sigma = \sum_i \sigma_i a_i + \sum_{i\leq j} \sigma_{ij} a_i a_j + \sum_{i\leq j\leq k} \sigma_{ijk} a_i a_j a_k + \ldots \tag{9}$$

Next, the subsystem embedding condition[12] is used to decouple the equations for the σ matrix elements from the equations for the S matrix elements. The working equations for the cluster matrix element S, ground state energy E_g and the cluster matrix elements σ are given by

$$\langle\Phi_e|H_1^{eff}|\Phi_0\rangle = 0, \tag{10}$$

$$\langle\Phi_0|H_1^{eff}|\Phi_0\rangle = E_g, \tag{11}$$

$$\langle\Phi_0|H_2^{eff}|\Phi_e\rangle = 0. \tag{12}$$

Here, Φ_e are the excited states, and H_1^{eff} and H_2^{eff} are the similarity transformed effective operators, defined as

$$H_1^{eff} = e^{-S}He^S \tag{13}$$

$$H_2^{eff} = e^\sigma e^{-S}He^S e^{-\sigma} \tag{14}$$

The effective Hamiltonians H_1^{eff} and H_2^{eff} are evaluated using the Baker-Campbell-Hausdorff expansion. We used a maximum of four-body expansion for both the cluster operator S and σ in Eqs. 8. Since the vibrational Hamiltonian with QPES has at-most four-body terms, the effective Hamiltonian H_1^{eff} and H_2^{eff} are also restricted to have up to four-body operators.

Finally, the coupled cluster linear response theory[13, 14] is used to calculate the vibrational excitation energies. In this approach, the effective Hamiltonian H_2^{eff} is diagonalized in the space of excited states of EHO. The excitation energies are obtained directly as the eigenvalues of H_2^{eff}. The configuration space for the H_2^{eff} is defined by the excited state space with at most four quanta in all the modes.

A. The second order vibrational perturbation theory

The second order vibrational perturbation theory (VPT2) is another popular method to calculate the anharmonic vibrational spectra of polyatomic molecules. Barone and co-workers[15–18] implemented a modified version of VPT2 method in Gaussian09. Here, the harmonic part of the Watson Hamiltonian is taken as zeroth-order Hamiltonian and the cubic and quartic terms are treated as perturbations. The working equation for the vibrational energy is given by

$$E(n) = \chi_0 + \sum_i \omega_i(n_i + \frac{1}{2}) + \sum_{i \leq j} \chi_{ij}(n_i + \frac{1}{2})(n_j + \frac{1}{2}) \tag{15}$$

Here, ω_i are the harmonic frequencies, n_i the vibrational states and χ_0 and χ_{ij} are the zero point contribution and anharmonic constants. These parameters are derived from the cubic, quartic and Coriolis coupling terms of the PES[15]. The working equation for the vibrational fundamentals transitions is[15]

$$\nu_i = \omega_i + 2\chi_i + \sum_{i \leq j} \chi_{ij}. \tag{16}$$

It was shown that the computation of the anharmonic constants χ_0 and χ_{ij} encounters singularities in the presence of strong vibrational resonances in the molecule. To overcome such singularity problem, a variational calculation is carried out with the states that are involved in the resonances[15, 18].

Table S1. The quartic force constants of bending modes of ethylene with different basis sets with RHF method (units are in cm^{-1}).

Basis set	F_{7777}	F_{4444}	$F_{11,11,11,11}$
6-311++G(3d,3p)	153	98	46
6-311+G(3d,3p)	152	98	48
6-311G(3d,3p)	160	95	51
6-311++G(2d,2p)	153	99	41
6-311G(2d,2p)	154	94	41
6-31++G(d,p)	151	102	41
6-31+G(d,p)	145	100	41
6-31G(d,p)	155	96	43
cc-pVDZ	156	96	41
aug-cc-pVDZ	128	104	45
cc-pVTZ	146	95	41
aug-cc-pVTZ	148	197	42

Table S2. The occupied molecular orbitals (OMO) of ethylene with different basis sets

| Basis set	HOMO (b_{3u})	OMO (b_{3g})	OMO (a_g)	OMO (b_{2u})	OMO (b_{1u})	OMO (a_g)
6-31G**	-0.370102	-0.502464	-0.580785	-0.636963	-0.788730	-1.027104
6-31+G**	-0.374333	-0.509599	-0.587655	-0.644106	-0.795466	-1.034369
6-31++G**	-0.374231	-0.509520	-0.587571	-0.644006	-0.795395	-1.034294
6-311G(2d,2p)	-0.374458	-0.506484	-0.585254	-0.642544	-0.791097	-1.031645
6-311+G(2d,2p)	-0.376173	-0.509940	-0.588832	-0.645954	-0.794552	-1.035179
6-311++G(2d,2p)	-0.376164	-0.509945	-0.588829	-0.645942	-0.794552	-1.035165
6-311G(3d,3p)	-0.374359	-0.506508	-0.585400	-0.641877	-0.791307	-1.031094
6-311+G(3d,3p)	-0.375806	-0.509843	-0.588683	-0.645101	-0.794567	-1.034282
6-311++G(3d,3p)	-0.375799	-0.509834	-0.588674	-0.645095	-0.794558	-1.034282
cc-pVDZ	-0.37155	-0.50200	-0.57902	-0.63460	-0.78636	-1.02633
aug-cc-pVDZ	-0.37323	-0.50697	-0.58329	-0.63924	-0.79154	-1.03019
cc-pVTZ	-0.37642	-0.50726	-0.58623	-0.64361	-0.79212	-1.03316
aug-cc-pVTZ	-0.37705	-0.50872	-0.58765	-0.64489	-0.79349	-1.03453
cc-pVQZ	-0.37765	-0.50819	-0.58779	-0.64521	-0.79298	-1.03485
aug-cc-pVQZ	-0.37782	-0.50875	-0.58831	-0.64563	-0.79349	-1.03528
ANO	-0.37788	-0.50837	-0.58803	-0.64530	-0.79306	-1.03489
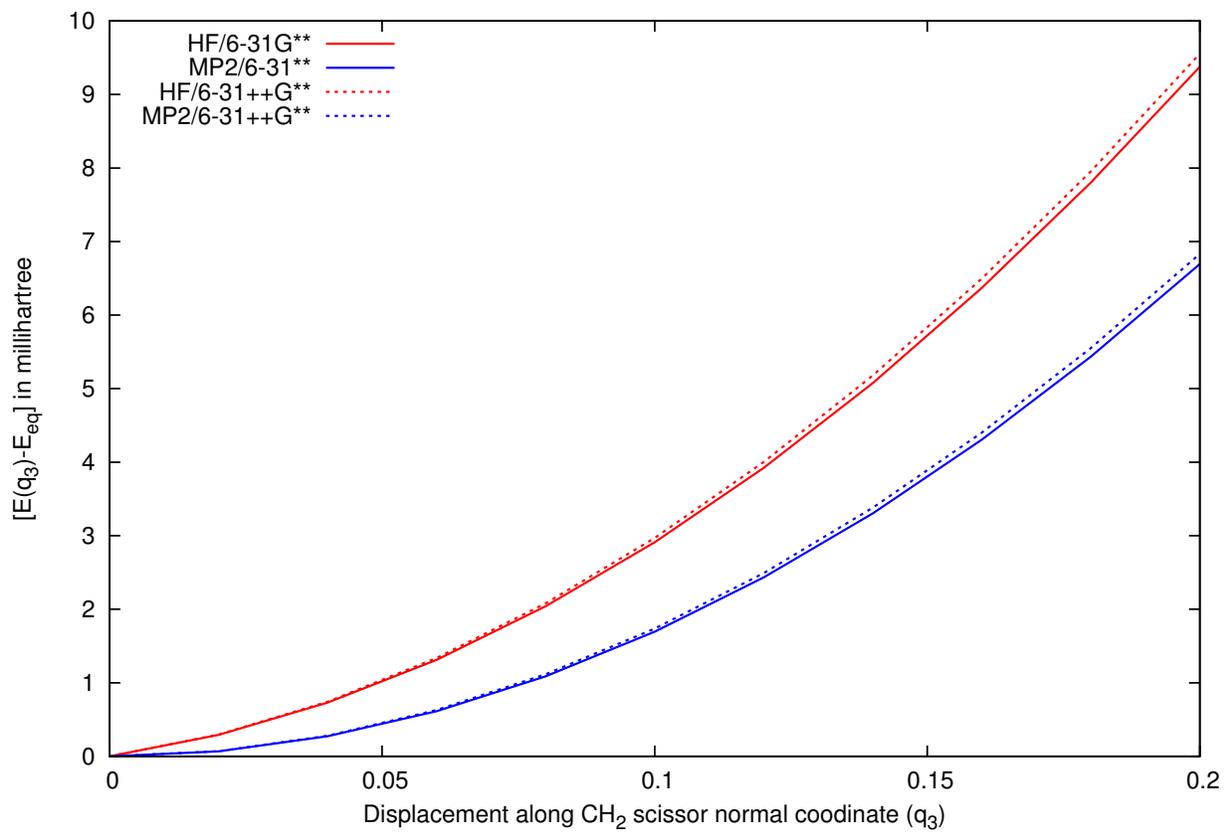
Figure S1. Changes of the RHF and MP2 energies with 6-31G** and 6-31++G** basis sets from the MP2 equilibrium along CH_2 scissor mode normal coordinate (q_3).
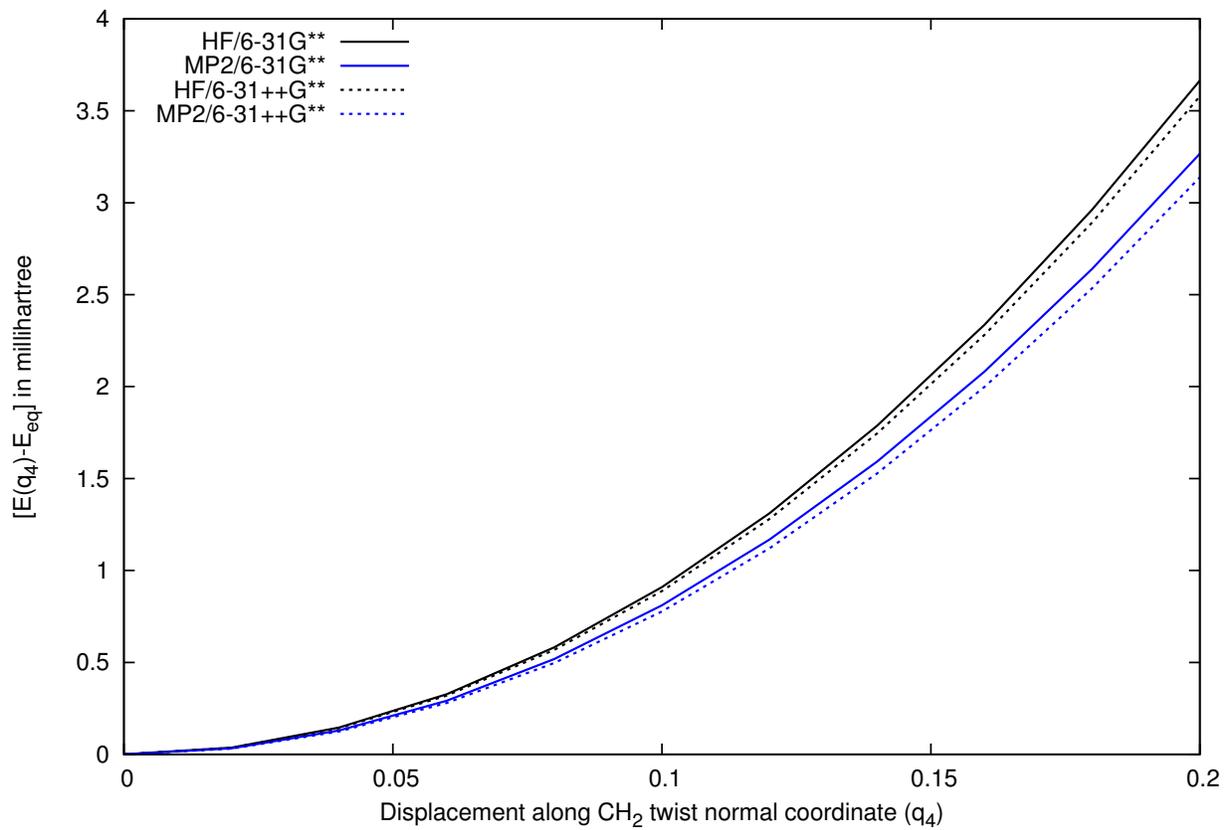
Figure S2. Changes of the RHF and MP2 energies with 6-31G** and 6-31++G** basis sets from the MP2 equilibrium along CH_2 twist mode normal coordinate (q_4).
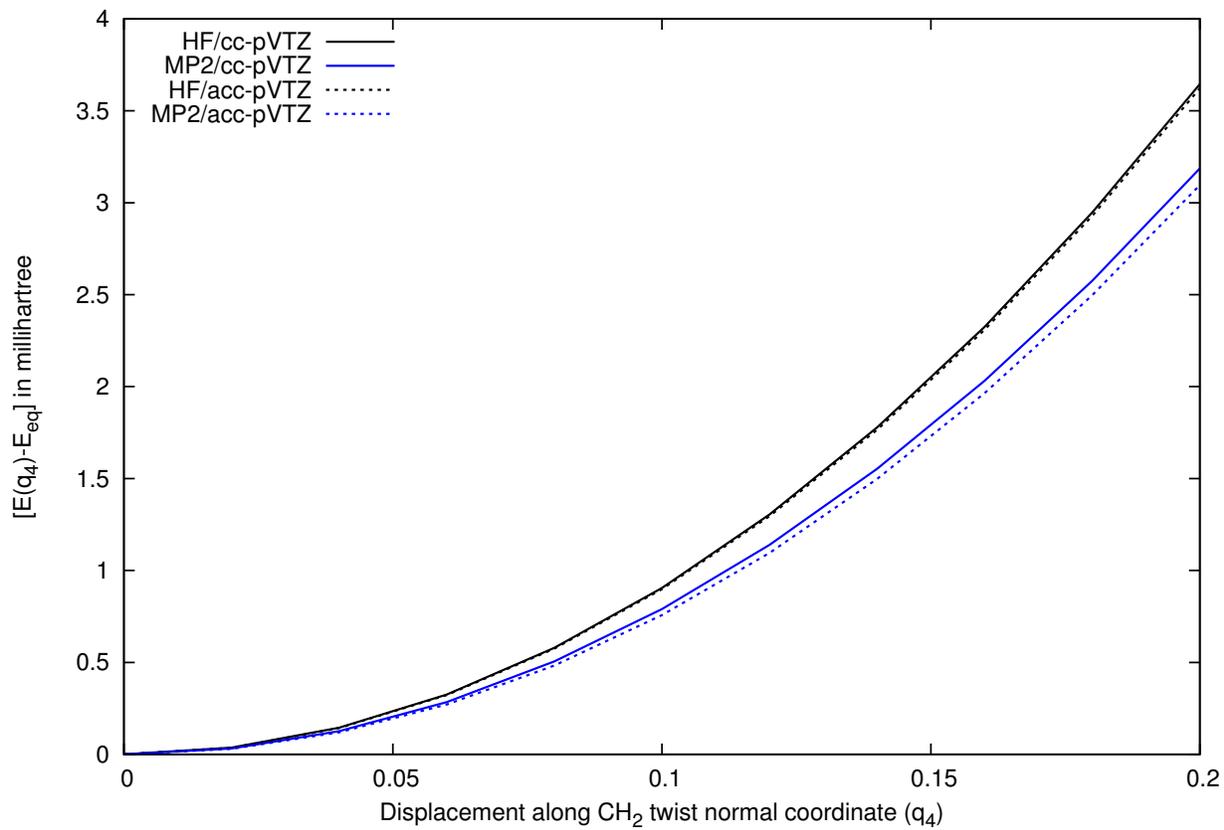
Figure S3. Changes of the RHF and MP2 energies with cc-pVTZ and aug-cc-pVTZ basis sets from the MP2 equilibrium along CH_2 twist mode normal coordinate (q_4).
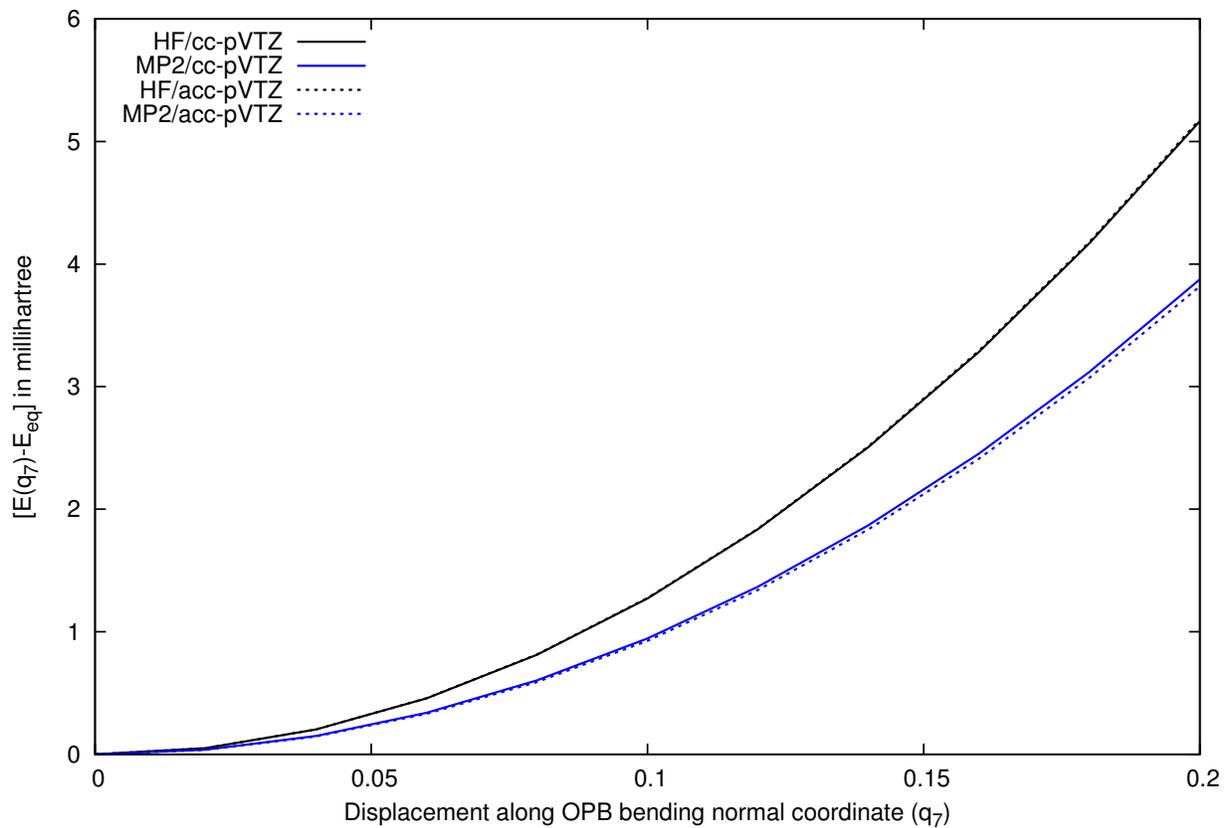
Figure S4. Changes of the RHF and MP2 energies with cc-pVTZ and aug-cc-pVTZ basis sets from the MP2 equilibrium along CH_2 wagging mode normal coordinate (q_7).
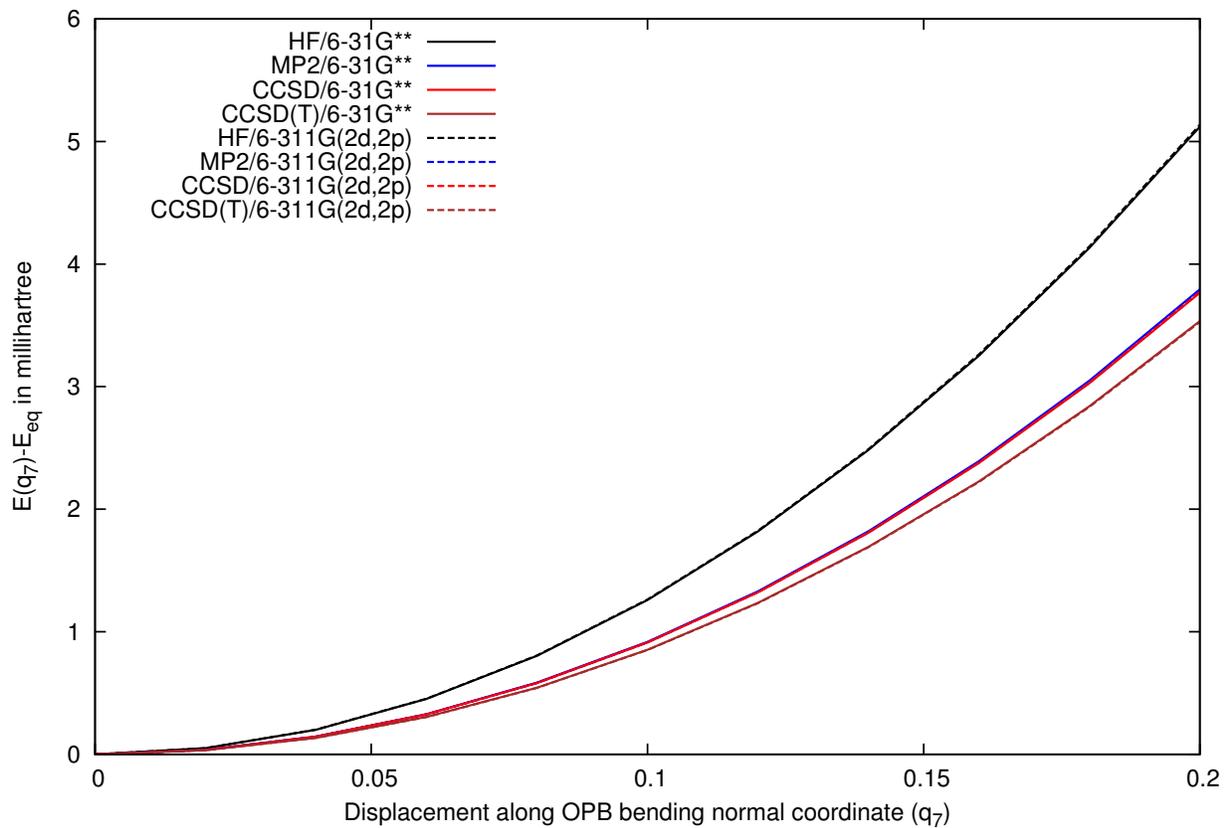
Figure S5. Changes of energies from equilibrium along out-of-plane bending mode normal coordinate (q_7) at the different level theories with the basis sets having no diffused function.
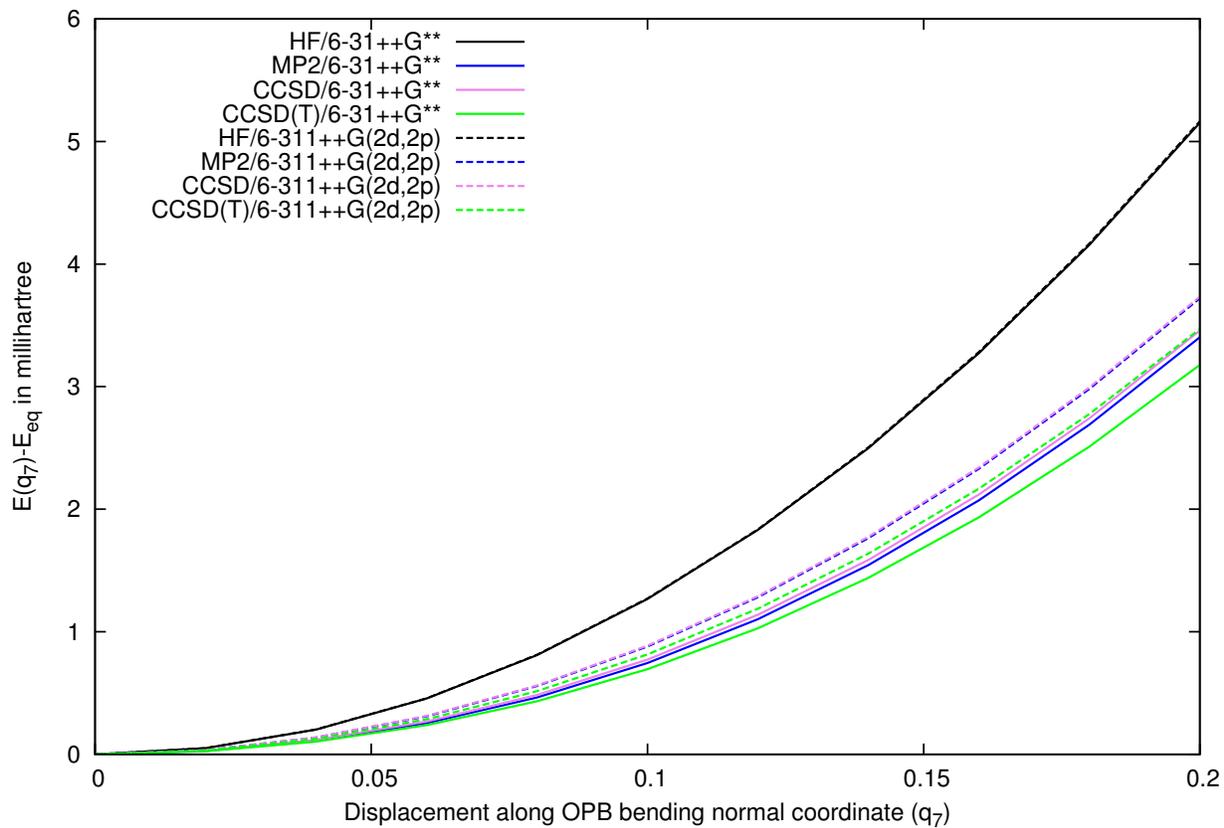
Figure S6. Changes of energies from equillibrium along out-of-plane bending mode normal coordinate (q_7) at the different level theories with the basis sets having diffused functions.

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