

**Response to “Comment on ‘Solvatochromic shifts of polar and non-polar molecules in ambient and supercritical water: A sequential quantum mechanics/molecular mechanics study including solute-solvent electron exchange-correlation’” [J. Chem. Phys.138, 217101 (2013)]**

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## Response to “Comment on ‘Solvatochromic shifts of polar and non-polar molecules in ambient and supercritical water: A sequential quantum mechanics/molecular mechanics study including solute-solvent electron exchange-correlation’” [J. Chem. Phys. 138, 217101 (2013)]

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In our recent work,<sup>1</sup> we investigated the water solvent effects on the electronic absorption of acetone and benzene under ambient and supercritical conditions through sequential quantum mechanics/molecular mechanics (QM/MM) calculations. Based on the detailed dependence analysis of the quantum mechanics (QM) region size in our QM/MM calculations, we reached a by-product conclusion in our work that the inclusion of the solvent molecules within the first solvation shell into the QM region to account for exchange interaction between a solute and its nearby solvents is especially vital for the highly accurate spectral shift calculations of non-polar solutes dissolved in water. Schwabe’s comment<sup>2</sup> raised disagreement with our conclusion and attributed the requirement for a large QM region to our insufficient electrostatic potential or neglect of polarization effect based on the fact that our employed  $\omega$ B97X-D functional<sup>3</sup> contains an empirical dispersion energy correction without direct couplings to electronic coordinates. Although Schwabe’s statement of  $\omega$ B97X-D is correct, we still consider that density functionals with (non-empiric) dispersion corrections are preferable for studying such systems with more specific physical concepts and cannot agree with their alternative interpretation of why a large QM region is needed to converge the results of aqueous benzene according to the following reasons.

In our original work,<sup>1</sup> we have examined the solvatochromic shift’s dependence on the embedding point charges and illustrated that QM/MM calculations with different point charge values will present qualitative similar descriptions for spectral shifts, although quantitative distinctions are noticeable. None of solute-only QM/MM calculations (QM solute surrounded by point charge solvents) are found to be able to correctly reproduce the red shift of aqueous benzene in our work. Here, we further examine other improved electrostatic potentials’ performances on the QM/MM calculation of aqueous benzene in which the dominant interactions between the solute and solvents are quantum dispersions. The effective fragment potential (EFP1) method<sup>4</sup> and the one-body fragment molecular orbital (FMO) method (FMO1)<sup>5</sup> with the

electrostatic potential (ESP), both of which include ground-state solvent polarization effect (polarization response of the solvents to the ground state of the solute), are implemented here for comparisons with QM/MM calculations with point charge embedding. We summarize the calculated results for acetone (benzene) in acetone + 36H<sub>2</sub>O (benzene + 36H<sub>2</sub>O) in Table I. From Table I, one may clearly see that solute-only QM calculations with different electrostatic potentials (SPC/E<sup>6</sup> point charge or EFP1 or ESP in FMO1) give quantitatively very close solvatochromic shift values, although both EFP and ESP in FMO can be considered as ground-state polarizable model potentials obtained from prior QM calculations without any empirical fittings and should be much superior to SPC/E point charge model. For hydrated benzene system, all these calculations except the full QM calculation present positive solvent shifts with close magnitudes for  $\pi \rightarrow \pi^*$  transition and cannot predict the qualitatively correct red-shift behavior.

It is well-known that including solvent polarizations in response to the solute excitation can further improve the description of solvent effects on electronic spectra.<sup>8–13</sup> Here, we also attempt to evaluate and analyze such effect. First, we performed preliminary QM calculations for both the ground and first excited states ( $S_0$  and  $S_1$ ) of acetone (benzene) + 36 nearest water molecules embedded in outer SPC/E point charges and then used the Mulliken charges of 36 nearest water molecules around the solute determined from the above preliminary QM calculations to mimic the solvent polarization in response to  $S_0$  or  $S_1$  of the solute. Then we performed solute-only QM calculations with these two different polarized potentials and used the energy difference between the excited state with solvent polarization upon solute excitation and the ground state with ground-state solvent polarization as the solute excitation energy with full solvent polarizations. Calculated solvatochromic shifts with such ground-state polarization and full polarization models as well as their differences are listed in Table II. Clearly, our results indicate very small solvent polarization effect (around 13 cm<sup>-1</sup>) upon solute excitation for aqueous acetone, in qualitative agreement with recent finding of Lin and Gao<sup>15</sup> that solvent charge redistribution following the solute electronic excitation contributes only a small correlation (0 to -37 cm<sup>-1</sup>) to the solvatochromic

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TABLE I. Calculated solvatochromic shift of acetone (benzene) in acetone (benzene) + 36H<sub>2</sub>O by solute-only QM calculations with different electrostatic potentials and full QM calculations at time dependent density functional theory (TDDFT) (LC-BLYP/6-31G(d)) level using GAMESS package.<sup>7</sup> The values in units of cm<sup>-1</sup> are statistically averaged from 100 uncorrelated configurations in our 2 ns molecular dynamics (MD) trajectories.<sup>1</sup>

	QM/MM (SPC/E)	FMO1	EFP1	Full QM
Acetone	1144	1269	1246	1375
Benzene	256	277	257	-536

shift of acetone in water. Simultaneously, one may also notice that solvent polarization effect upon solute excitation for benzene (around 16 cm<sup>-1</sup>) is slightly larger than that for acetone (around 13 cm<sup>-1</sup>). Therefore, also considering the fact that the total solvatochromic shift of benzene is much smaller in magnitude than that of acetone, one may conclude that such effect is more important for benzene than acetone, as has been elucidated in recent work of Sneskov *et al.*<sup>13</sup> that solvent polarization effects upon solute excitation are more significant for  $\pi \rightarrow \pi^*$  excitations than  $n \rightarrow \pi^*$  excitations. However, solute-only QM/MM calculations can not predict the qualitatively correct red-shift behavior for aqueous benzene, even full solvent polarization effect is included. Therefore, we consider further including the full solvent polarization effect is still insufficient for describing the excited states of such systems in which dispersion as a quantum correlation effect dominates the interactions between the solute and solvents.

In view of the above facts that results by both simple point charge embedding and ground-state polarizable EFP and FMO methods deviate much from the experimental determinations for aqueous benzene and solvent polarization in response to the solute excitation for such a system is also very small, we conclude that only improving the Coulombic electrostatic potential and including solvent polarization effect are

TABLE II. Calculated solvatochromic shift of acetone (benzene) in acetone (benzene) + 36H<sub>2</sub>O by solute-only QM calculations with different solvent polarization models at TDDFT (LC-BLYP/6-31G(d)) level using GAUSSIAN 09 program.<sup>14</sup> The values in units of cm<sup>-1</sup> are statistically averaged from 100 uncorrelated configurations in our 2 ns MD trajectories.<sup>1</sup>

Solvent polarization model	Ground-state polarization	Full polarization	$\Delta$
Acetone	1282	1295	13
Benzene	264	280	16

not sufficient for correctly describing the excited states of systems in which dispersions dominate the interactions between the solute and the solvents. Under such circumstance, further treatment of the non-Coulomb component of dispersion interactions becomes necessary, and enlarging the QM region size and incorporating new exchange repulsion potentials in QM/MM calculations will be reasonable choices for including solute-solvent exchange interactions which contribute to the quantum correlation nature of dispersion. It should be mentioned that it is not a new finding and previously other groups<sup>16–19</sup> also addressed the importance of exchange interaction (Pauli repulsion, non-Coulombic interaction) in embedding calculations for molecular properties. Therefore, we reconfirm that the inclusion of the solvent molecules within the first solvation shell into the QM region to account for exchange interaction between a solute and its nearby solvents is highly recommended for accurate electronic spectral shift calculations of non-polar solutes dissolved in water.

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