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Linear Response Properties of Liquid Water Calculated Using CC2 and CCSD within Different Molecular Mechanics Methods[†]

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In this paper we present linear response properties of liquid water calculated using the second-order approximate coupled cluster singles and doubles (CC2) and the coupled cluster singles and doubles (CCSD) wave function parametrizations combined with different molecular mechanics models. We discuss different approaches within the QM/MM scheme where the solvent molecules are represented by point charges and induced dipole moments. Here, we address two important aspects in QM/MM methods. First, we aim at obtaining MM parameters from an iterative self-consistent approach. Second, we show how to reduce the computational costs of the models considerably without reducing the quality of the results. Excitation energies, transition moments, and oscillator strengths are compared within the different approaches. Finally, we report the CC2 frequency dependent polarizability compared to the CCSD results.

I. Introduction

In the theoretical ab initio description of solute−solvent problems the size of most systems makes it impossible to perform a complete quantum mechanical description of the entire system. As a first approach, a few solvent molecules can be included in the QM calculation neglecting all long-range solute−solvent interactions. The disadvantage of such supermolecular calculations is that even for strongly truncated systems the calculations are still very computationally demanding. On top of this it is sometimes difficult to extract the properties of the individual molecules from the supermolecular results and additional approximations have to be applied. Supermolecular calculations are usually performed on an optimized geometry, and no statistics are therefore accounted for in the calculations.

Most theories describing a condensed phase divide the system into parts describing a smaller part with quantum mechanics and the major part by a classical description. A simple model is to represent the surrounding medium as a dielectric continuum and thereby implicitly include a statistical average over the solvent configurations, and this approach has been applied in many variations by different groups.[1−8] However, no solvent structure is included in the dielectric medium model, and the model is therefore not capable of representing important solvent interactions such as hydrogen bondings. Extending the quantum mechanical system by including a limited number of solvent molecules leads to an improved model, the semicontinuum model,[2,9] but these models have similar problems as the supermolecular methods in extracting specific molecular properties.

A straightforward improvement of the quantum mechanical/classical picture from the simple dielectric medium model is to keep the discrete structure of the solvent and represent the solvent molecules through molecular mechanical (MM) parameters defining the quantum mechanical/molecular mechanical (QM/MM) model. A model like this has the potential capability of giving a proper description of hydrogen bonds. Since the first model of this kind was presented by Warshel et al.[10] a number of models have been presented in the literature combining semiempirical electronic structure methods,[11−13] ab initio uncorrelated[14−17] and correlated[17−23] methods, and density functional theory[24−27] with molecular mechanics. Some of these models combine the dielectric continuum model and the QM/MM model surrounding the MM part with a dielectric continuum,[14,15,26] and Gao and Alhambra have used Ewald summation to get a proper bulk description.[13]

The usual representation of the MM medium in QM/MM models is at least to include atomic point charges and in some cases induced electric moments. The van der Waals interactions are usually modeled with a Lennard-Jones potential.

Another area where QM/MM methods have been heavily used is in the description of biomolecular structures where the molecules become so large that a full quantum mechanical description becomes practically impossible. Using a QM/MM method the chemically interesting part of the system is represented using quantum mechanics, and the rest of the system is represented using molecular mechanics. Here, additional complications of representing the covalent bonds between the QM and the MM parts of the system arise. For recent developments of QM/MM methods describing biomolecular problems the reader should consult the review articles given in refs 28 and 29.

Investigations have shown that for polar solvents such as water induced dipole moments have to be included to get a proper description of the solute−solvent interactions.[17,20−22] As the QM/MM model depends on the parameters used, the determination of MM parameters of high quality is crucial in order to obtain a reliable representation of a system. In this paper we present a method for determining the partial charges and isotropic polarizability of water from the QM/MM results. The quality of the parameters from such an approach depends on the descriptions of the QM system and the QM/MM-coupling.

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In vacuum studies the dynamically correlated coupled cluster (CC) approach[30] has successfully been applied to give high quality results of molecular properties. The CC hierarchy of CC models CCS, CC2,[31] CCSD,[32] and CC3,[33] which converges fast toward the Full Configuration-Interaction (FCI),[34] allows for a systematic increase of accuracy in the description of the electronic structure of a molecular system at the expense of increasing computational cost.

We have recently combined the CC electron structure theory with MM in a CC/MM model[20,21,23,35,36] representing the MM part through partial charges and isotropic polarizabilities. The CC/MM model has been implemented for the CC2 and CCSD electronic structure methods. Recent studies have indicated a successful reproduction of experimental data for the liquid phase using the CC/MM approach,[21,35,36] in accord with the well-established high accuracy of the CC method in vacuum studies. When combining coupled cluster and molecular mechanics an important task becomes the reduction of the computational cost, and in ref 20 we obtained a considerably reduction of this from seeking an optimal iterative procedure for determining the CC/MM wave function parameters. Similar, in ref 22, we found that we could limit the surrounding solvent to include only a minor part of the full solvent water cluster to obtain accurate results.

In this paper we show how to determine the liquid MM partial charges and isotropic polarizability from the QM water molecule by an iterative self-consistent procedure within the CC/MM approach. Second, we discuss how many polarizable water molecules have to be included in the CC/MM model in order to reproduce the results of a fully polarized solvent. We compare excitation energies, transition properties, the polarizability tensor elements and the frequency dependence of the isotropic polarizability obtained from standard parameters,[37] and full polarization of the solvent with the results from CC/MM calculations using the iterative determined MM partial charges and isotropic polarizability. Finally, we compare results obtained using the CC2 and CCSD methods.

II. Method

A. The CC Hierarchy. Within the CC wave function parametrization a number of models have been developed in order to approximate the Full Configuration-Interaction (FCI) wave function. The straightforward hierarchy of approaches including single excited configurations CCS(N^4), singles and doubles excited configurations CCSD(N^6)[32] etc. has been extended with the second-order approximate coupled cluster singles and doubles model CC2(N^5)[31] and the approximate singles doubles and triples model CC3(N^7).[33] The numbers in parentheses are the scaling of the computation within the model where N is the number of basis functions. The iterative CC hierarchy, CCS, CC2, CCSD, and CC3, provides a systematic extension for including a larger fraction of electron correlation into the wave function converging toward the FCI wave function.[34]

Within the CC2 method the singles equations are the CCSD expressions, whereas the doubles equations are approximated to be correct to first order only (with singles treated as zeroth order parameters due to their importance for describing the response to external perturbations). The advantage of the CC2 model is the reduced N^5 scaling with respect to the number of basis functions compared to the N^6 scaling of the CCSD model. Therefore, the CC2 model provides the possibility of calculating general frequency dependent molecular properties and electronic excitation energies and transition properties with this reduced cost.

B. The CC/MM Model. For the coupled cluster/molecular mechanics method we refer to our work presented in refs 20, 21, and 23. In short, we surround the QM system, described by a CC wave function, with a MM medium represented as atomic point charges q_s at positions $\vec{R}_s$ and induced dipole moments μ_a^{ind} at positions $\vec{R}_a$ (which here are the centers of mass of the solvent molecules). The total Hamiltonian consists of three terms, according to

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{QM/MM} + \hat{H}_{MM} \tag{2.1}$$

where the first term is the vacuum Hamiltonian, the second term is the QM/MM interaction Hamiltonian, and the last term corresponds to the MM energy. The second term is given by

$$\hat{H}_{QM/MM} = \hat{H}^{el} + \hat{H}^{pol} + E^{vdw} \tag{2.2}$$

The last term in eq 2.2, the van der Waals contribution (E^{vdw}), is modeled by a 6−12 Lennard-Jones potential and depends only on the nuclear geometry of the system. The second term gives the polarization interactions (induction energy) between the induced dipoles in the MM system and the electric fields from the QM system, and the first term describes the electrostatic interactions between the QM system and the partial charges.

The CC/MM method is defined by the introduction of a so-called variational Lagrangian.[38] The variational Lagrangian for the CC/MM method is obtained by adding the individual energy contributions related to eq 2.2 to the expression for the Hamiltonian in eq 2.1 and introducing the CC expression for the expectation values.[20,23] The optimization conditions for the CC/MM wave function are derived by requiring the Lagrangian to be stationary with respect to both the so-called amplitudes and multipliers of the model.[20,23]

The response functions from which we calculate molecular properties are obtained as derivatives of the time-averaged CC quasi-energy $\{L(t)\}_T$.[38] For a derivation of the linear response function including the CC/MM terms the reader is referred to ref 21, and for further information on the CC response theory the reader is referred to ref 38. From the linear response functions we are able to obtain a plenitude of molecular properties, such as, excitation energies and transition probabilities for one photon processes and frequency-dependent polarizabilities.

III. Computational Details

All calculations have been performed using a local version of the DALTON program[39] containing the additional implementation of the CC/MM model. We have used the correlation consistent basis sets of Dunning[40,41] and from previous investigations of basis set dependencies we have chosen to use the d-aug-cc-pVTZ[63] (daT) [6s5p4d3f] basis set when comparing models since this has been shown to give a proper description of the ground-state QM system as well as for the excited states and the molecular properties studied here.[20,21,23] In the investigation of the time saving procedure of excluding polarization of the solvent molecules beyond a certain distance from the QM system in section IV A 2 we have used the aug-cc-pVQZ [6s5p4d3f2g] basis set. The use of a large basis set ensures in addition to high accuracy that the I/O load versus the CPU load on the machine is small, and we are able to perform direct CPU-time comparisons between the different computational setups.

The geometry of the QM water molecule used in all calculations is taken from ref 42 using $R_{OH} = 0.9572$ Å and $\angle_{HOH} = 104.47°$. The QM water molecule is placed in the XZ-

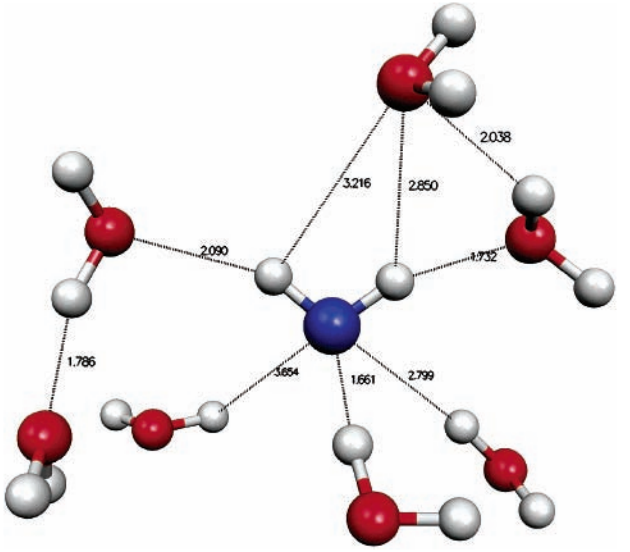

Figure 1. The geometry of the water molecules in the water cluster with a center of mass within a distance of 4 Å from the QM water molecule center of mass. The blue water molecule is the QM system and the red water molecules are the MM particles.

plane with the oxygen atom in the origin of the coordinate system and the C_2-axis in the Z direction.

The QM/MM calculations have been performed using a single average water configuration defined upon MD simulations. The average structure is defined using statistical (Boltzmann) sampling over 8000 trajectories each of a simulation time of 20 ps started from the same equilibrated geometry with different initial velocities.[42] The potential used is a polarizable (1,6,12)-potential with parameters of Ahlström et al.[37] $q_H = 0.3345$, $q_O = -0.669$, $\bar{\alpha} = 9.718$, $\sigma_O = 5.983$, and $\epsilon_O = 0.00025$ in atomic units (au). The simulation box-length was 15.5 Å, and the box contained 128 rigid water molecules with the intramolecular geometry of ref 42, previously discussed. We applied periodic boundary conditions and used a spherical cutoff distance of 10 Å. The temperature and pressure were kept constant during the simulation at 298 K and 1 atm, respectively.

In a QM/MM calculation we take one water molecule as the QM system, and the rest of the cluster defines the MM part of the system which we represent with the same parameters as used in the MD simulation unless stated otherwise. We note that using an average geometry is a simplified way of accounting for a statistical mechanics sampling of the different solvent configurations. This provides a single number instead of a statistical distribution. However, as the scope of this work is to compare the ability of the different methods to reproduce each other we have chosen to use the average geometry method simplifying the comparison of the calculated properties considerably.

To illustrate the structure around the QM water molecule in the water cluster we have in Figure 1 shown the QM water molecule (the blue molecule) and the MM water molecules (the red molecules) within a center of mass−center of mass distance of 4.0 Å from the QM system. From Figure 1 it is seen that two outgoing and one ingoing hydrogen bonds lie within 2 Å. At distances around 2.8 Å one additional ingoing and one additional outgoing hydrogen bond are included. The structure clearly shows a hydrogen bonding stabilization of the QM water molecule from the solvent as it should for a polar solvent−solute system, and the structure therefore shows the expected geometry around of the solvated QM water molecule.

IV. Results and Discussion

A. The CC/MM Methods. In this section we discuss two important aspects of QM/MM methods. First, we present a method for determining the partial charges and isotropic polarizability of the MM molecules from the QM molecule by a self-consistent iterative procedure. This means that given a particle structure we are able to determine the parameters for water (not the Lennard-Jones parameters) from the QM/MM method alone independently of classical fitting procedures, and the solution will only depend on the wave function and the QM/MM interaction terms. The nonmeasurable partial charges are determined from the calculated total dipole moment, whereas the molecular polarizability is obtained directly from the CC/MM calculation.

From the CC/MM method we obtain high quality electron-correlated parameters, and we are able to represent the solvent−solute system as identical water molecules in the sense that the MM parameters are determined from the CC description of a water molecule. We note that the method is an extension of the procedure presented in ref 21 for the self-consistent determination of the MM isotropic polarization parameter from CCSD/MM linear response.

Second, we discuss a method for reducing the computational costs of the computation while still maintaining the high quality of the calculation. This aspect is extremely important especially when considering our recently developed CC/MM method.[20−23] In this nonvariational wave function parametrization we introduce a coupling between the CC amplitudes and the Lagrangian multipliers which increases the computational costs, compared to the vacuum CC method where amplitudes and multipliers are uncoupled. Since the vacuum CC method is a computational demanding method by itself, this aspect becomes very important for the efficiency of the CC/MM method.

1. The Iterative Self-Consistent CC/MM Method. Within a linear approximation the *i*th component of the total dipole moment μ_i^{tot} of a single water molecule is given as

$$\begin{aligned}\mu_i^{tot} &= \mu_i^{perm} + \mu_i^{ind}\\ &= \mu_i^{perm} + \sum_j \alpha_{ij} E_j^{tot}\end{aligned} \tag{4.3}$$

where μ_i^{perm} is the *i*th component of the permanent dipole moment, α_{ij} is the *ij*th component of the dipole−dipole polarizability tensor, and E_j^{tot} is the *j*th component of the total electric field. From the CC/MM response theory we obtain the total dipole moment and the dipole−dipole polarizability tensor,[21,43] and the electric field is given by classical expressions for charges and dipole moments.[20] Note that we calculate the electric field in the QM center of mass as we represent the MM water molecules with an isotropic polarizability placed in the center of mass.

Restraining the partial charges on the atomic sites to reproduce the permanent dipole moment given as $\mu_i^{perm} = \sum_{s=1}^{S} q_s r_{s,i}$ we find that eq 4.3 can be rewritten to an expression for the partial charges. Due to the C_{2v}-symmetry of water and the relation $2q_H = -q_O \equiv q$ between the charges we are able to obtain a simplified expression for q. Placing the water molecule in the *xz*-plane, with the C_2-axis along the *z*-axis and the oxygen atom placed in the origin of the coordinate system, the *x* and *y* components of the permanent dipole moment are constraint to be zero by symmetry. Using an isotropic polariz-

TABLE 1: Iterative Determination of the Partial Atomic Charges (au) and the Isotropic Polarizability (au) of Liquid Water Using the CC/MM Model[a]

model	it. no	q	$\bar{\alpha}$	$E_{CC/MM}$	μ_z
CC2	0	0.6690	9.7180		
CC2	1	0.6005	10.6416	−0.042803	2.721
CC2	2	0.6011	10.7052	−0.037994	2.667
CC2	3	0.6008	10.7100	−0.038150	2.669
CC2	4	0.6008	10.7104	−0.038140	2.670
CC2	5	0.6008	10.7104	−0.038140	2.670
CCSD	0	0.6690	9.7180		
CCSD	1	0.6232	9.9717	−0.042670	2.720
CCSD	2	0.6245	9.9840	−0.038898	2.675
CCSD	3	0.6244	9.9849	−0.039026	2.677
CCSD	4	0.6244	9.9850	−0.039027	2.677
CCSD	5	0.6244	9.9850	−0.039027	2.677

[a] The calculations have been performed using the d-aug-cc-pVTZ basis set. In the nth iteration the charges and polarizability from iteration $n - 1$ have been used as input. Also included in the table are the CC/MM interaction energy, $E_{CC/MM}$ (hartree), and the z component of the total dipole moment (Debye), μ_z, from which the partial charges are determined.

ability for water we obtain that the charge q is given by the expression

$$q = \frac{\mu_z^{tot} - \bar{\alpha} E_z^{tot}}{z_H} \tag{4.4}$$

where z_H is the z component of the distance vector to hydrogen which is the same for both hydrogen atoms in the given orientation. We note that the use of an isotropic polarizability is not a limitation of the model, and a sum as in eq 4.3 may be used. However, the use of an isotropic polarizability is a good approximation for water and it simplifies the expression.

Starting from a given set of partial charges and isotropic polarizability (this can also be zero as in a vacuum) we obtain a new set of parameters for the MM system which we use as input. The procedure is repeated until convergence is reached for both parameters.

In Table 1 we have collected the results obtained within the CC2/MM and CCSD/MM methods from the above procedure starting from the parameters of Ahlström et al.[37] used in our previous calculations for liquid water.[20−23,43] The results in Table 1 are obtained using the daT basis set. The charges of Ahlström et al. are constrained to reproduce the experimental value of the permanent dipole moment of gas-phase water (1.85 D[44]). From Table 1 we see that the converged parameters obtained from the CCSD/MM method are closer to the starting parameters than those obtained by the CC2/MM method both concerning the partial charges and the isotropic polarizability. For both CC/MM models the partial charges are decreased compared to the starting values by 7−10%, and the isotropic dipole−dipole polarizability is increased by 3−10%.

In ref 22 we investigated the effects of variations of each of the parameters on the CCSD/MM calculated excitation energies and isotropic polarizability of liquid water. We found that decreasing the magnitude of q results in a decrease of the calculated excitation energies, whereas the calculated isotropic polarizability is increased. The same effect was observed when increasing the $\bar{\alpha}$ parameter. However, the calculated values were found to be much more sensitive to changes in the charges than in the polarizability.

From this observation we expect that the CC/MM model, using the optimized parameters from Table 1, produces excitation energies which are smaller and isotropic polarizabilities which are larger compared to the results obtained with the CC/MM model using the parameters of Ahlström et al. However, the CC2/MM results should be more affected than the CCSD/MM results. This is also what we observe in sections (IV B 1) and (IV B 2). We will refer to the CC/MM model using the optimized parameters from Table 1 as CC/MM(it-sc).

Another way to determine the partial charges would be to use the method of Cioslowski[45,46] which has been used in combination with a heterogeneous solvation model to represent the solute−solvent interaction through mirror charges obtained by this approach.[47] The charges obtained by the Cioslowski method do not reproduce the permanent dipole moment as the CC/MM(it-sc) does, but the method is general and applicable to all systems and not only to water and a few other molecules which the CC/MM(it-sc) method is limited to.

2. Reducing the Computational Costs of the CC/MM Method. In this section we discuss the initial implementation of a consistent screening procedure in the CC/MM method. We have introduced the ability to have different classical models in the MM medium. We have investigated the mixture of a simple point-charge (SPC) model together with an extended simple point-charge (SPC-E) model which includes an isotropic polarizability. The point charges enter the CC optimization conditions in a relatively nonexpensive way, so the computationally expensive part of the CC/MM method is the inclusion of the induced dipole moments.

We have investigated the effect of including the polarization effects through an isotropic polarizability on the MM water molecules within a given radius from the QM water molecule. The MM water molecules outside the radius are represented only through point charges. The radius is calculated as the distance between the centers of mass of the QM and the MM systems. All calculations have been performed with the CCSD/MM model using the aug-cc-pVQZ (aQ) basis set and the MM parameters of Ahlström et al.[37]

In Figure 2 the setup of a calculation including both atomic partial charges and a center of mass point polarizability on the MM water molecules within a distance of 6.0 Å is illustrated. The MM water molecules at greater distances are represented only through atomic point charges. In Figure 2 the blue water molecule is the QM system, the red water molecules are the MM part of the system including both atomic partial charges and a point polarizability, and the yellow water molecules are the MM part of the system represented only through atomic point charges.

In Figure 3 the CC/MM interaction energy, $E_{CC/MM}$, is plotted as a function of the radius within which an isotropic polarizability is included in the MM potential. From Figure 3 we note that the polarization of the MM medium cannot be neglected as considerable effects are observed when including $\bar{\alpha}$ in the calculation (no polarization is for a zero distance). This has also been reported in ref 20 where comparisons were made between a nonpolarizable (nonpol) solvent and a polarizable (pol) solvent. However, from Figure 3 we note that the calculated energy converges very fast when including more polarizable solvent molecules, and for a distance of approximately 6.0 Å the energy has converged to within 0.2% of the value obtained using a fully polarized solvent. From Figure 3 we note that including the first solvation shell of 4 water molecules, which correspond to a radius of 3.5 Å, is not enough to reproduce a fully polarized solvent, and we have to include at least a second solvation shell corresponding to approximately 6.0 Å on the figure.

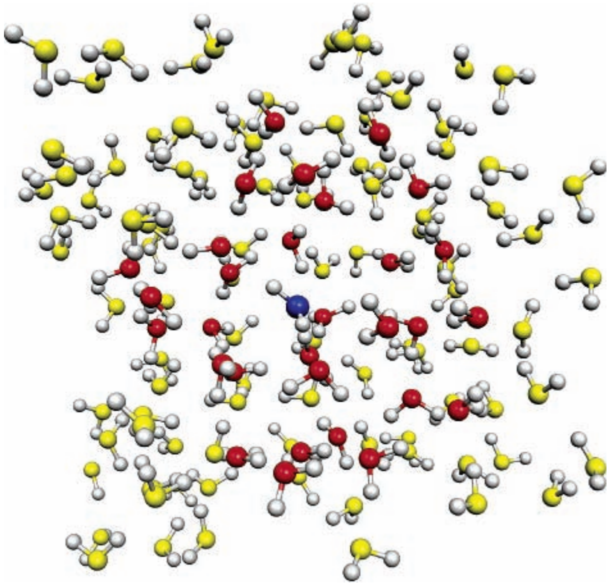

Figure 2. The geometry of the full water cluster illustrating the setup of the method combining different models in the MM part of the system. Here, the blue molecule is the QM system, and the red water molecules are MM molecules represented by partial charges at the atomic sites and a point polarizability in the center of mass. The yellow water molecules are MM molecules represented only through partial charges on the atomic sites. The figure shows the setup for a calculation including a point polarizability on MM water molecules with a center of mass within a distance of 6 Å from the QM center of mass.

In Figure 3 we observe that $E_{CC/MM}$ is not yet fully converged at 6.0 Å as the energy is decreased further when going to 7.0 Å. However, at 8.0 Å the energy becomes larger again, and at 9.0 Å and larger distances it is converged to an energy similar to the one obtained at 6.0 Å. The reason for this is that center of mass distances are used to determine whether a molecule is represented with a polarizability in addition to the point charges. This means that molecules with the oxygen pointing toward the QM system are included before molecules with the hydrogens pointing toward the QM system. At 6.0 Å the molecules included are distributed in a homogeneous way around the QM water molecule. At 7.0 Å the distribution of polarizable MM molecules becomes inhomogeneous as the additional molecules are mainly added in two directions. At 8.0 Å some of the homogeneous character is reestablished, and at 9.0 Å the distribution is homogeneous again. At larger distances it is seen that the inhomogeneous distribution of the polarizable MM molecules becomes less important as the energy has converged. We note that the change in $E_{CC/MM}$ is only 0.5 mHartree when going from 6.0 to 7.0 Å.

The same trend is observed in Figure 4 which shows the z component of the total dipole moment as a function of the radius within which the MM molecules are polarized. As reported in ref 43 the CC/MM(nonpol) method (when the distance is zero in Figure 4) underestimates the dipole moment. But as for the CC/MM interaction energy the value is seen to converge very fast and including polarizable solvent molecules within a distance of 6.0 Å the value of μ_z reproduces the one of the CC/MM(pol) method within 0.1%.

In Figure 5 we have plotted the 4 lowest excitation energies as a function of the radius within which an isotropic polarizability is included in the MM potential. We note that the inclusion of polarization in the MM medium has less effects on the results and as reported in ref 21 the CC/MM(nonpol) method gives results that are less than one tenth of an electronvolt larger in best cases than the ones of the CC/MM-(pol) method. However, we note that excluding the polarization from the solvent water molecules the order of the excitation energies changes as the third and fourth excited state changes place in the spectrum. To obtain the right order it is crucial to include polarizable solvent water molecules beyond the first solvation shell. Including polarizable water molecules within a distance of 6.0 Å from the QM water molecule the right order is obtained, and the results deviate less than 0.2% from the pol results.

In Figure 6 the isotropic polarizability of the QM molecule calculated at four different frequencies is plotted as a function

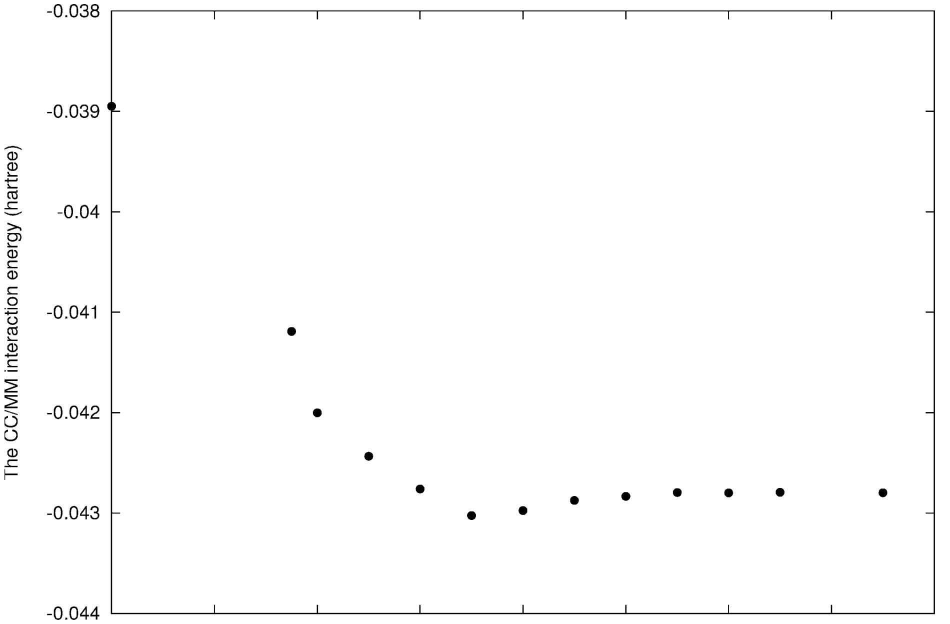

Figure 3. The CC/MM interaction energy (hartree) as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules. The energy has been calculated using the CCSD/MM model and the aug-cc-pVQZ basis set.

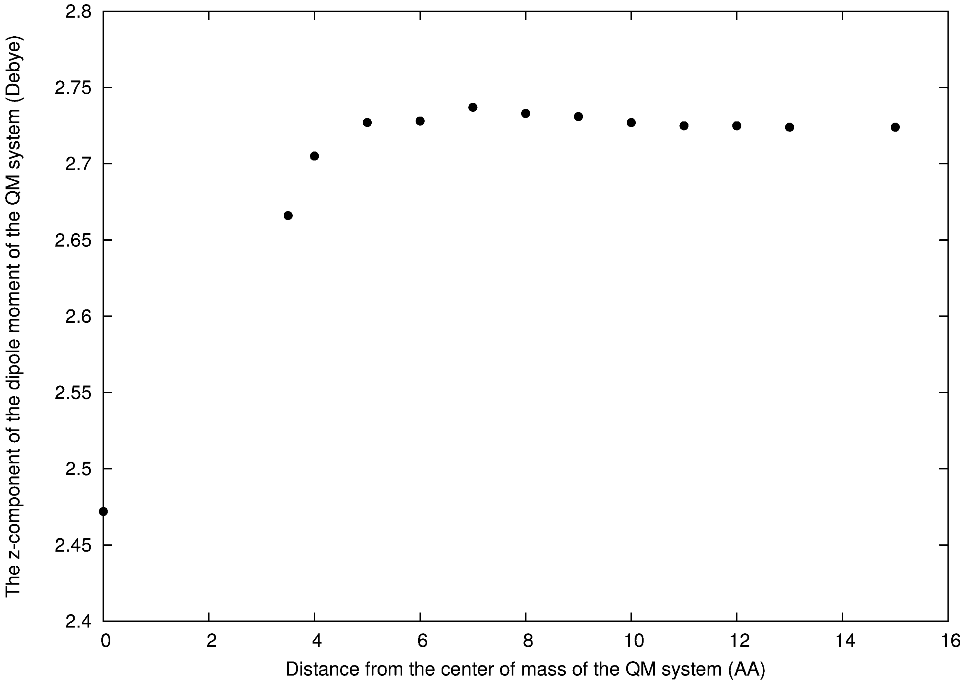

Figure 4. The *z*-component of the dipole moment (Debye) as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules. The dipole moment has been calculated using the CCSD/MM model and the aug-cc-pVQZ basis set.

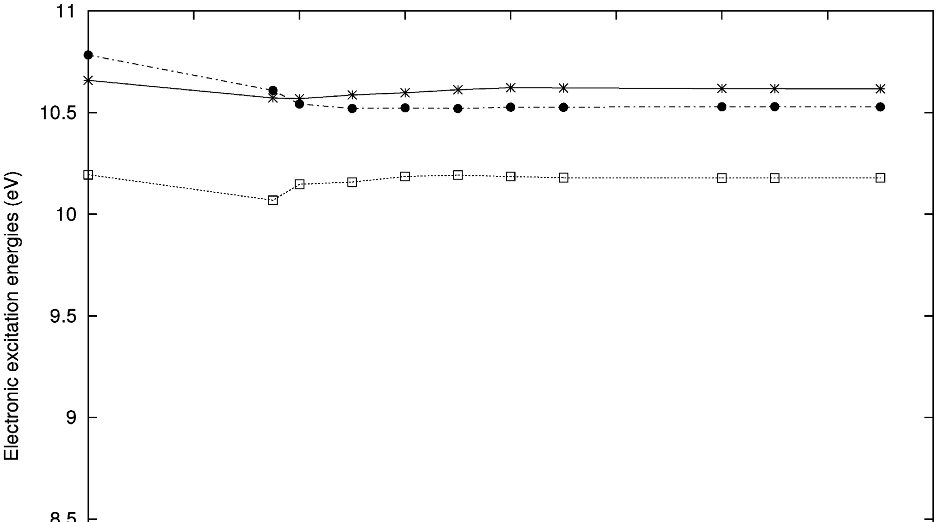

Figure 5. The excitation energies (eV) of the 1^1B_1, 1^1A_2, 2^1B_1, and 2^1A_1 transitions as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules. The energies have been calculated using the CCSD/MM model and the aug-cc-pVQZ basis set. $1b_1 \rightarrow 3s$: (− − × − −), $1b_1 \rightarrow 3p_y$: (···□···), $3a_1 \rightarrow 3s$: (—∗—) and $1b_1 \rightarrow 3p_z$: (− · − ● · − ·).

of the radius within which polarizable solvent water molecules are included. In agreement with the observations in ref 21 we find that the nonpol method underestimates the isotropic polarizability compared to the results obtained from the pol method. Similar to the previous discussed physical properties the results are seen to converge toward the pol results very quickly when including polarizable solvent molecules into the calculation. Including polarization within a distance of 6.0 Å the calculated isotropic polarizabilities reproduces the pol method results within 0.1%. The observations made in Figures 3−6 agree with a previous study of the hyperpolarizability of liquid water using a semicontinuum model where a first solvation shell was not enough alone to give a proper description of the first hyperpolarizability.[9]

In the CC/MM(nonpol) method the MM partial charges enter the equations in a nonexpensive way as the CC amplitudes and multipliers are decoupled as in the vacuum case. This means that the amplitudes can be optimized without reference to the multipliers, and only in order to obtain first or higher order properties the multipliers are needed. To obtain a set of

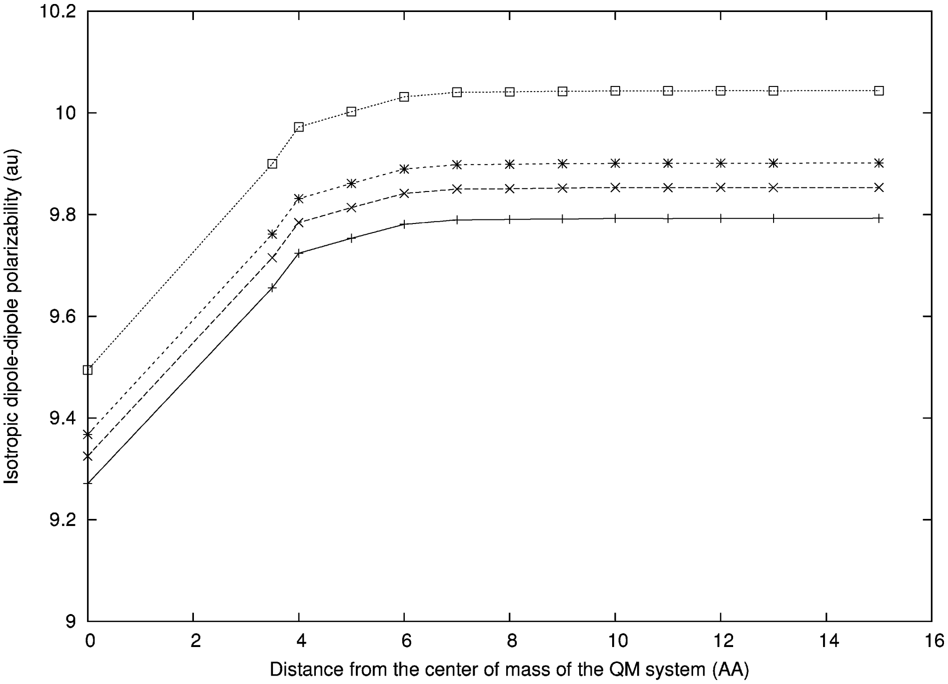

Figure 6. The isotropic polarizability (au) calculated at the frequencies 0.000 au (—+—), 0.0428 au (— — × — —), 0.0570 au (- -∗- -). and 0.0856 au (···□···) as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules. The calculations have been performed using the CCSD/MM model and the aug-cc-pVQZ basis set.

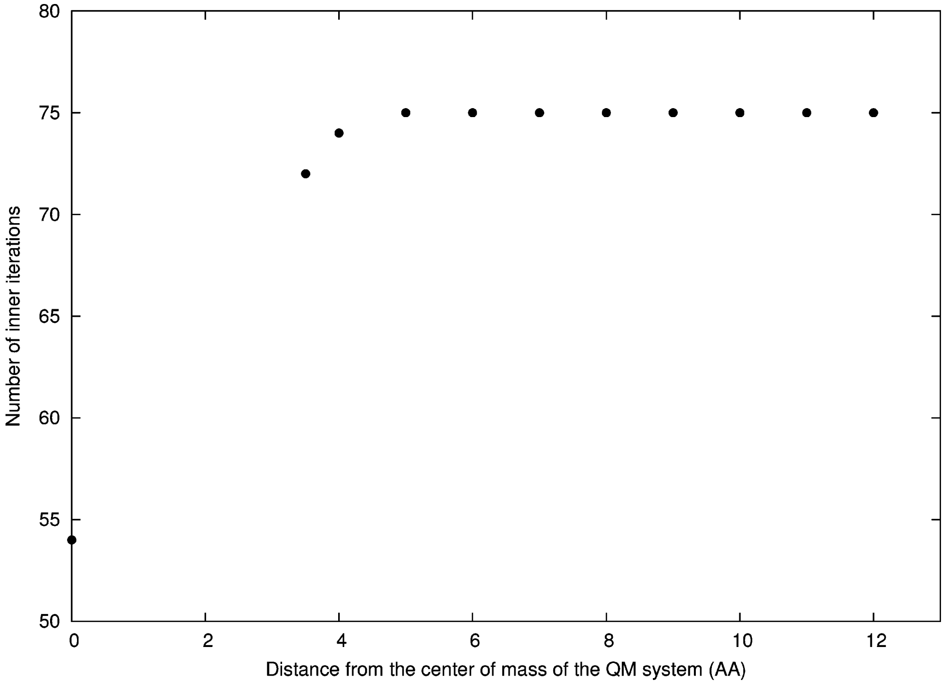

Figure 7. The number of inner iterations in a CCSD/MM calculation as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules.

optimized multipliers the optimized amplitudes are used. However, introducing the polarization of the MM system a coupling of the CC amplitudes and multipliers is introduced, and the amplitudes cannot be determined independently of the multipliers. This means that the CC parameters are found from an iterative procedure using the amplitudes to determine a set of multipliers which is used to determine a new set of amplitudes until convergence is reached. In ref 20 we found a considerable saving of the computational time when only iterating a few steps in the determination of the amplitudes before proceeding to iterate a few steps in the determination of the multipliers.

In Figure 7 we have plotted the number of inner iterations, N_{it}, needed for the results to converge to a given threshold in the CC/MM code. The term N_{it} relates to the total sum of iterations used in both the solution of the CC amplitudes, multipliers, and intermediate steps. We have chosen an optimal number of iterations in the amplitude solver and the multiplier solver of 3 and 4, respectively, minimizing N_{it} in the fully polarized model.[20] This explains that the number of inner iterations does not explode in Figure 7 when polarization is introduced in the calculation but is less than doubled when going from a pure SPC description to one including polarizable water

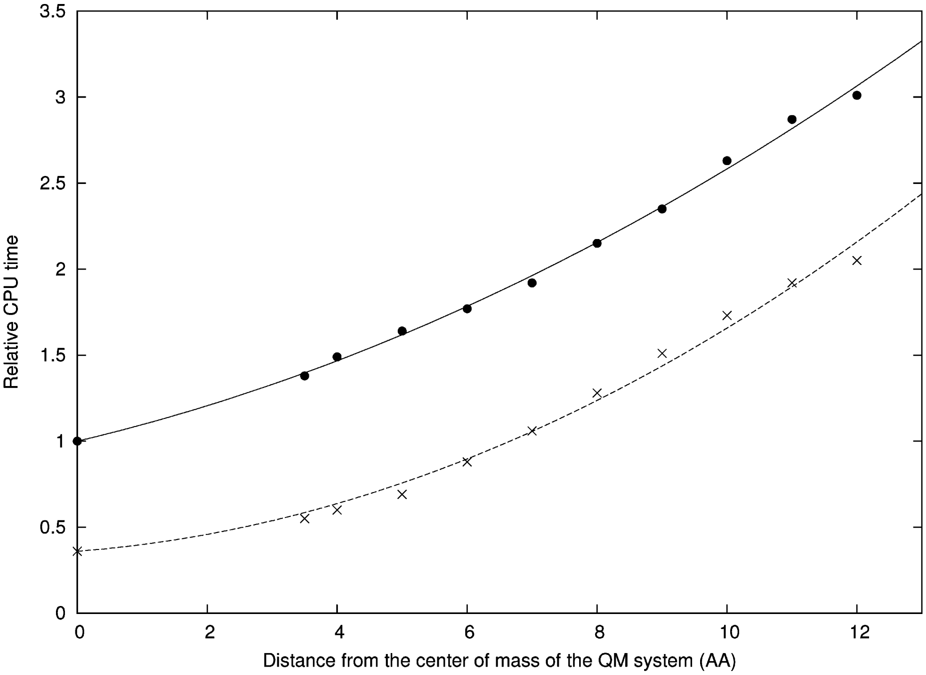

Figure 8. (— ● —): The relative CPU-time of CCSD/MM calculations as a function of the distance from the center of mass of the QM system within which a point-polarizability has been placed at the center of mass of the MM molecules. The time is relative to the fastest calculation representing all MM molecules with a SPC model. The calculations of the ground-state energy, dipole moment, 8 excitation energies, corresponding transition moments, and oscillator strengths and the frequency dependent polarizability at 4 different frequencies are performed using the aug-cc-pVQZ basis set. For comparison the CPU-time (relative to the CCSD/MM(nonpol) calc.) for identical CC2/MM calculations has been shown (- - - × - - -).

molecules in the first solvation shell (on the water molecules within a distance of 3.5 Å). However, the effect of including a first solvation shell of polarizable water molecules is still considerable as the number of inner iterations is increased by 33%. In Figure 7 it is seen that the number of inner iterations converge to a constant number when introducing polarization beyond the first solvation shell.

The constant number of iterations seen in Figure 7 when polarizing beyond the first solvation shell does not mean that the CPU-time used in the calculation is kept constant. In Figure 8 we have plotted the CPU-time of CCSD/MM calculations, including a point-polarizability on the water molecules within a given distance from the QM center of mass, relative to the CPU-time of a similar calculation using the nonpol method. We note that the increase in relative CPU-time is proportional to R^2 where R is the distance within which polarizable solvent molecules are included. This is plausible as the number of particles included in a sphere scales quadratically with the radius of the sphere when the density is constant ($dN = \rho dV \propto R^2$).

For comparison, the CPU-time, relative to the corresponding CCSD/MM(nonpol) CPU-time, has been plotted in Figure 8 for CC2/MM calculations. The CC2/MM model exhibits the same quadratical dependence in R as the CCSD/MM model does. However, we note that the N^5-scaling of the CC2 method makes the computation much quicker than the corresponding CCSD calculation, which scales as N^6. For water a reduction of the CPU-time by more than a factor of 2 is seen when comparing the relative CPU-times of the CCSD/MM and CC2/MM calculations where polarized water molecules have been included within a distance of 6.0 Å. The reduction in CPU-time for CC2 compared to CCSD depends on the size of the QM system and the number of basis functions. It should be noted that for CC2 the relative effect in CPU-time of introducing polarized solvent molecules is larger. For $R = 12$ Å the CC2/MM CPU-time is almost 6-fold larger than for the nonpolarized CC2/MM calculation, while the corresponding CCSD/MM number is roughly 3. This is because the CC/MM terms have a computational scaling of N^5 and thus have accounted for a relative larger fraction of the CPU-time for CC2 compared to CCSD.

From the above discussion we find that using a mixed model including polarizable water molecules within a radius of 6.0 Å and a simple SPC model for all MM water molecules at larger distances we reduce the computational time by almost a factor of 2 compared to the fully polarized solvent model. However, the results of the energies and physical properties obtained using this model deviates less than 0.2% from the pol model. We will refer to this model as CC/MM(pol/spc).

B. The CC/MM Results. In the present section we discuss the linear response properties of liquid water obtained from the different CC/MM models discussed in the previous section. We have calculated the three lowest excitation energies, the corresponding transition moments and oscillator strengths, and the frequency dependent polarizability tensor elements. We have already presented these quantities of liquid water in ref 21 using our most expensive model, the fully polarized CCSD/MM(pol) model with the Ahlström parameters and the d-aug-cc-pVTZ basis set. In this paper we will focus on two aspects: (i) The ability of different CC/MM approaches to reproduce the CC/MM(pol) results but at a lower computational cost or with parameters obtained from the QM/MM calculation itself. (ii) How well the CC2/MM methods compare with the computationally more expensive CCSD/MM methods. Finally, we compare the CC/MM results with other and less expensive methods and experiments.

The reason that we use the CCSD/MM(pol) results from ref 21 as reference data is as follows: (i) The CCSD model accounts for a larger part of the electronic correlation than the CC2 model and is therefore a more accurate model. (ii) The MD simulation from which the mean configuration has been constructed has been run using the same classical parameters of Ahlström et al.

TABLE 2: Excitation Energies (eV), Corresponding Transition Moments (au), and Oscillator Strengths of Water Calculated Using the d-aug-cc-pVTZ Basis Set[a]

	$1b_1 \rightarrow 3sa_1$						$1b_1 \rightarrow 3pb_2$						$3a_1 \rightarrow 3sa_1$					
method	E_{ex}	TMx	TMy	TM_z	OS	ΔE_{ex} [b]	E_{ex}	TMx	TMy	TMz	OS	ΔE_{ex} [b]	E_{ex}	TMx	TMy	TMz	OS	ΔE_{ex} [b]
CC2(vacuum)	7.249	0.000	0.554	0.000	0.054		8.888	0.000	0.000	0.000	0.000		9.664	0.000	0.000	0.600	0.085	
CC2/MM(pol)	7.761	0.001	0.647	0.004	0.080	0.515	9.432	0.013	0.152	0.033	0.006	0.544	10.165	0.066	0.078	0.662	0.112	0.501
CC2/MM(pol/spc)	7.734	0.003	0.639	0.005	0.077	0.485	9.421	0.053	0.038	0.037	0.001	0.533	10.136	0.069	0.073	0.650	0.107	0.472
CC2/MM(it-sc)	7.744	0.002	0.650	0.001	0.080	0.495	9.390	0.018	0.198	0.024	0.009	0.502	10.134	0.058	0.076	0.669	0.113	0.470
CCSD(vacuum)[c]	7.616	0.000	0.524	0.000	0.051		9.368	0.000	0.000	0.000	0.000		9.881	0.000	0.000	0.491	0.058	
CCSD/MM(pol)[c]	8.176	0.000	0.627	0.002	0.079	0.560	9.965	0.009	0.149	0.017	0.006	0.597	10.556	0.053	0.075	0.654	0.113	0.675
CCSD/MM(pol/spc)	8.153	0.003	0.621	0.003	0.077	0.537	9.955	0.015	0.176	0.009	0.008	0.587	10.541	0.055	0.070	0.644	0.109	0.660
CCSD/MM(it-sc)	8.171	0.000	0.628	0.001	0.079	0.555	9.944	0.016	0.145	0.015	0.005	0.576	10.555	0.046	0.072	0.655	0.113	0.674
HF/MM(pol)[d]	9.49		0.601			0.84	11.3		0.068			1.0						
MCSCF/MM(pol)[d]	8.62		0.654			0.77	10.5		0.129			0.9						
DFT/DRF[e]	8.25				0.075	0.53	10.18				0.003	0.65	10.27				0.112	0.59
experiment[f]	8.2					0.8	9.1						9.9					0.2

[a] The CC/MM results are presented within the different CC/MM schemes discussed in the text. [b] $\Delta E_{ex} = \Delta E_{ex}^{liquid} - \Delta E_{ex}^{vacuum}$. [c] Results from ref 21 using the d-aug-cc-pVTZ basis set. [d] Results from ref 17 using the aug-cc-pVQZ basis set. [e] Results from ref 27 using the shape-corrected SAOP potential and a large even-tempered basis set of Slater type orbitals including 69 and 28 basis functions on oxygen and hydrogen, respectively. For further details on the potential and the basis set see ref 27. [f] References 50, 60, and 61.

as are used in the CCSD/MM(pol) calculations, and therefore the results have been obtained in a consistent way. One could argue that the CCSD/MM(it-sc) model is the most accurate of the models as the parameters are obtained from the CCSD/MM model itself. However, for consistency in the procedure we have chosen to use the same parameters as in the MD simulation for reference data.

The CCSD/MM(it-sc) model is very useful when using an SPC set of parameters, like the frequently used TIP3P,[48] for the MD simulations to obtain the system configurations. The use of (1,6,12) potentials makes the MD simulation considerably quicker than using a polarized potential. However, it has been shown in several studies that the polarizability cannot be neglected from the QM/MM calculations.[17,20−22] Here, the it-sc model can be used to generate partial charges and polarizabilities from the structures, constructed using the SPC parameters, to use in the QM/MM calculations.

1. Excitation Energies and Transition Properties of Liquid Water. In Table 2 we have collected excitation energies and the corresponding transition properties of the $1b_1 \rightarrow 3sa_1$, $1b_1 \rightarrow 3pb_2$, and $3a_1 \rightarrow 3sa_1$ transitions in liquid water calculated using the different CC/MM approaches from the previous section and the daT basis set. For comparison Table 2 also contains the CCSD/MM(pol) results from ref 21 using the same basis set. First, comparing the vacuum excitation energies in Table 2 we find that the CC2 results underestimates the CCSD results by as much as 0.5 eV (for the $1b_1 \rightarrow 3pb_2$ transition), whereas the CC2 transition moments are generally overestimated by a few percent. We note that even though the CC2/MM results deviate from the CCSD/MM results they do so in a consistent way meaning that the same trends observed from the CCSD/MM calculations are also observed from the CC2/MM calculations. However, this occurs at a much lower computational cost making the CC2/MM method preferable for some purposes.

Comparing the different MM representations within a given CC wave function approximation we find that the changes are much more moderate than the ones observed for the different coupled cluster approaches. Comparing the CC/MM(pol) and the CC/MM(pol/spc) models we find that the excitation energies deviate less than 0.5% for both CC methods, and therefore we also observe similar solvation shifts of the states in the CC/MM(pol) and CC/MM(pol/spc) models. Comparing the CC/MM(pol) and CC/MM(pol/spc) transition properties we observe that the CC/MM(pol/spc) method reproduces the CC/MM(pol) results. However, one deviation is found when comparing the *TMy* results for the vacuum dipole forbidden $1b_1 \rightarrow 3pb_2$ transition obtained with the CC2/MM(pol) and CC2/MM(pol/spc) models. It is seen that the TM_y result of the CC2/MM(spc/pol) model is five times smaller than the corresponding value from the CC2/MM(pol) model. This is not observed in the CCSD case.

The reason is that the excited state corresponds to a $3p_y$ Rydberg state (extended in the Y direction) and that it is more diffuse in the CC2 description than in the CCSD description. As we have discussed in previous papers on the CC/MM model the lack of short range repulsion in the optimization conditions of the wave function allows the electrons to occupy space which potentially would be occupied by the electrons of the MM molecules including these in a QM description.[20,21,43] Therefore, the CC/MM wave function is allowed to diffuse into the MM medium, and the CC2 state which is more diffuse reaches further into the MM medium than the corresponding CCSD state. As only the first two solvent shells are polarized in the CC/MM-(pol/spc) model the polarization effects are especially underestimated in the Y direction compared to the CC/MM(pol) model. However, the underestimation is a result of an artifact in the CC/MM model and not in general an error of the pol/spc approach. Therefore, we conclude that the CC/MM(pol/spc) method is able to reproduce the results of the much more expensive CC/MM(pol) method to a satisfactory degree of accuracy.

Comparing the CC/MM(it-sc) and the CC/MM(pol) excitation energies in Table 2 we find the CC/MM(it-sc) results to be decreased by less than 0.5%. However, the CC2/MM(it-sc) results are decreased more than the CCSD/MM(it-sc) results which is in perfect agreement with our previous discussion in section(IV A 1) from the observations made in ref 22. Comparing the transition moments and oscillator strengths obtained by the CC/MM(pol) and CC/MM(it-sc) models we find that the CC/MM(it-sc) method reproduces the CC/MM(pol) results within a few percents. We conclude that the parameters obtained by the iterative self-consistent procedure represent the MM medium to a similar degree of accuracy as the parameters of Ahlström et al. concerning the excitation energies.

In Table 2 the excitation energies calculated using other representations of the QM part of the system are reported. A direct comparison can be made as the same mean structure of the water cluster has been used in all cases. First, we note that the total neglect of electronic correlation in the HF/MM method leads to deviations by more than one eV toward larger energies compared to the CCSD/MM(pol) method. Also the solvent shifts are found to be as much as 70% larger than for the CCSD/MM methods. The static correlated MCSCF/MM method deviates by about 0.5 eV from the CCSD/MM results. The deviations are of the same size as observed for the CC2/MM methods. However, the MCSCF/MM method tends to overestimate the excitation energies, whereas the CC2/MM methods tend to underestimate them. The MCSCF/MM solvent shifts are as much as 50% larger than the CCSD/MM results, whereas the CC2/MM solvent shifts deviate within 10%.

The DRF/DFT approach using the SAOP exchange correlation potential[49] compares well with the CCSD/MM results both concerning the excitation energies, the oscillator strengths, and the solvent shifts. However, the values reported here are the best results from ref 27 using the nonstandard correlation SAOP potential. A number of potentials including several standard potentials have been tested, and the calculated excitation energies deviate by as much as 2 eV from the CCSD/MM models, and the results generally show a large dependence of the potential used.[27] Using the standard BLYP potential the excitation energy of the $1b_1 \rightarrow 3sa_1$ transition has been calculated to 6.49 eV with a solvent shift of 0.25 eV[27] and compares even worse than the HF/MM method with the CCSD/MM results.

In Table 2 we have reported the experimentally determined maximum absorptions, ϵ_{max}, for the $1b_1 \rightarrow 3sa_1$ and the $3a_1 \rightarrow 3sa_1$ transitions which are the values that can be compared best with the calculated vertical excitation energies. We find that the CCSD/MM models show excellent agreement with experiment on the location of the lowest excitation energy, whereas the solvent shift is a little lower than the experimental value. This is because the CCSD calculated vacuum excitation energy differs by 0.2 eV from the experimental value of 7.4 eV.[50] The CCSD/MM results overestimate the second excitation energy by as much as 0.8 eV and the third by half an eV. This is probably due to the total neglect of short-range repulsion in the CC/MM model causing the diffuse excited states to be too much affected by the solvent as the electrons are allowed to be located in space formally occupied by the electrons of the solvent molecules.[21] This might also explain the relatively larger effect on the more diffuse $3pb_2$ state than the $3sa_1$ state.

Concerning the CC2/MM models we find the first excitation energy to be underestimated by almost half an eV and the excitation energies of the second and third transition to be overestimated by about 0.3 eV. We find that the CC/MM models using both CC2 and CCSD are able to reproduce the relatively large oscillator strength of the $1b_1 \rightarrow 3sa_1$ transition and the larger oscillator strength of the $3a_1 \rightarrow 3sa_1$ transition as observed in the experiments.

2. The Frequency Dependent Polarizability of Liquid Water. In Table 3 we have collected the diagonal tensor elements of the static polarizability tensor, the isotropic polarizability, and the anisotropy, and in Table 4 we show the parameters obtained from fitting the frequency dependent isotropic polarizability to a $\bar{\alpha}(\omega) = A(1 + B\omega^2)$ expression. The polarizabilities in Tables 3 and 4 have been calculated in a vacuum and using the different CC/MM methods discussed previously, and all calculations have been performed using the daT basis set. Note that we have omitted the off-diagonal elements of the polarizability tensor in Table 3. These are nonzero using one configuration but are zero using correct statistical averaging over a number of configurations.

First, concerning the vacuum results in Table 3 we find that the polarizability, obtained using the CC2 wave function parametrization, have larger tensor components and isotropic polarizability than those from the CCSD approach. However, the anisotropy of the CC2 model is smaller than for the CCSD model. The reason is that the diagonal elements of the CCSD model deviate more internally than the CC2 elements do which results in a larger anisotropy (see definition in footnote in Table 3). The larger CC2 polarizability is intuitively understood from a sum over states expression for the static polarizability in which products of transition moments belonging to the same excited state is divided by the corresponding excitation energies. From Table 2 we observed that the CC2 excitation energies were smaller than the CCSD excitation energies, whereas the transition moments were more alike. This results in larger contributions from these states to the CC2 polarizability in the sum over states expression compared to the corresponding CCSD terms.

The same trend is observed concerning the CC/MM results in Table 3. The CC2/MM polarizability results are larger than the corresponding CCSD/MM results showing that it is easier to polarize the liquid CC2 water molecule than the liquid CCSD water molecule. The anisotropy on the other hand is reversed compared to the vacuum case as the CC2/MM calculated anisotropies are larger than the corresponding CCSD/MM results. From the definition of the anisotropy in the footnote of Table 3 and the tensor components of the polarizability tensor

TABLE 3: Diagonal Components of the Static Polarizability Tensor, the Isotropic Polarizability, and the Anisotropy (All in au) Calculated with the d-aug-cc-pVTZ Basis Set and the CC2 and CCSD Wave Function Approximations within the Different CC/MM Schemes Discussed in the Text

model	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\bar{\alpha}$[a]
CC2	10.155	10.524	10.280	10.320	0.326
CC2/MM(pol)	10.294	10.862	10.769	10.642	1.223
CC2/MM(pol/spc)	10.284	10.857	10.747	10.629	1.215
CC2/MM(it-sc)	10.396	10.901	10.834	10.710	1.168
CCSD	9.353	9.978	9.613	9.648	0.544
CCSD/MM(pol)[b]	9.774	10.011	10.130	9.972	1.057
CCSD/MM(pol/spc)	9.765	10.006	10.110	9.961	1.048
CCSD/MM(it-sc)	9.817	10.006	10.132	9.985	0.998
MCSCF[c]	9.74	9.15	9.36	9.42	
MCSCF/MM(pol)[c]	9.54	9.72	9.82	9.70	
DFT[d]	9.88	8.92	9.52	9.44	
DFT/DRF[d]	9.80	9.55	9.85	9.73	

[a] The anisotropy is defined as $\Delta\bar{\alpha} = \sqrt{(D_1 + 6O_1)/2}$ where $D_1 = (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2$ and $O_1 = (\alpha_{xy}{}^2 + \alpha_{xz}{}^2 + \alpha_{yz}{}^2)$. [b] Results from ref 21 using the d-aug-cc-pVTZ basis set. [c] Results from ref 17 using the aug-cc-pVQZ basis set. [d] Results from ref 27 using the shape-corrected SAOP potential and a large even-tempered basis set of Slater type orbitals including 69 and 28 basis functions on oxygen and hydrogen, respectively. For further details on the potential and the basis set see ref 27.

TABLE 4: Parameters (au) for the Expression $\bar{\alpha}(\omega) = A(1 + B\omega^2)$ Giving the Frequency-Dependency of the Isotropic Polarizability[a]

model	A	B	asymptotic standard error
CC2	10.320	4.134	±0.036
CC2/MM(pol)	10.642	4.099	±0.035
CC2/MM(pol/spc)	10.629	4.111	±0.027
CC2/MM(it-sc)	10.710	4.142	±0.028
CCSD	9.648	3.672	±0.023
CCSD/MM(pol)	9.972	3.660	±0.025
CCSD/MM(pol/spc)	9.961	3.664	±0.025
CCSD/MM(it-sc)	9.985	3.670	±0.023

[a] The parameters are found by fitting the expression to the analytical values calculated using the d-aug-cc-pVTZ basis set within the coupled cluster models discussed in the text.

listed in Table 3 we observe that the large deviation between the α_{xx}-component and the two other diagonal components in the CC2/MM case causes the anisotropy to be larger than in the CCSD/MM case. The off-diagonal elements (not shown) and difference between the α_{yy} and α_{zz} components are similar in the two CC/MM models, so these contributions to the anisotropy are much the same in the CC2 and CCSD cases.

Comparing the tensor components within the different CC/MM methods for a given CC wave function we see from Table 3 that both the CC/MM(it-sc) and CC/MM(pol/spc) models reproduce the CC/MM (pol) results to a high degree of accuracy. Especially, we note that the CC/MM (pol/spc) model is able to account for the polarization of the solvent, and the model gives almost identical results to the CC/MM(pol) model at a much lower computational cost. The results obtained for the CC/MM-(it-sc) model show that we are able to determine parameters which provide results of the same quality as the ones obtained in previous studies with the parameters of Ahlström et al.[21] We note that both the CCSD/MM and CC2/MM models predict that the polarizability becomes larger when going from vacuum to liquid.

In Table 3 we have collected the tensor elements of the static polarizability of liquid water as calculated with other QM/MM models. Again a direct comparison can be made as the same water cluster mean structure has been used in these studies. From Table 3 it is seen that the MCSCF/MM method underestimates all the diagonal elements of the tensor compared to the CCSD/MM results which lead to an underestimation of the isotropic polarizability. The tensor components as well as the isotropic polarizability as calculated with the DFT/MM method compares well with the CCSD/MM models showing only minor differences. However, as was the case when comparing excitation energies the DRF/DFT method is very dependent on the potential used. For an example, using the standard BLYP potential one obtains $\bar{\alpha} = 11.39$.[27] It is difficult to compare the anisotropies from refs 17 and 27 with the ones obtained from the CC/MM models as another definition has been used. We prefer to report the anisotropy invariant as defined in the footnote of Table 3 as this is invariant to any orthogonal transformation (e.g. rotation of the molecular axis) of the polarizability tensor.[51]

From Table 4 the frequency dependence of the isotropic polarizability in a vacuum is seen to be more pronounced in the CC2 case than the CCSD case (the *B* parameter). This is also the case when comparing the CC/MM results of liquid water. We note that the dispersion is almost identical in gas phase and in liquid phase using both CC2 and CCSD. Again we find the CC/MM(pol/spc) model to give almost identical results as the CC/MM(pol) model. The parameters obtained from the iterative self-consistent procedure lead to a little more polarized CC wave function with a little more frequency dependency than the wave function obtained using the parameters of Ahlström et al. Comparing the frequency dependence of the CC/MM models with the MCSCF/MM[17] and the DRF/DFT[27] methods we find in all cases that the isotropic polarizability is increased with increasing frequency.

Experimentally, the gas-phase static polarizability has been found from a quadratic extrapolation of the refractive index at 8 frequencies between 0.068 au and 0.095 au to $\alpha_{vac}^{exp}(0.00) = 9.83$ au[52] and using the Lorenz−Lorentz equation[53] the polarizability has been calculated from the refractive index at 0.088 au to $\alpha_{vac}^{exp}(0.088) = 9.92 \pm 0.02$ au.[54] The CC results for the gas-phase polarizability agrees with experimental results to a high accuracy when corrected for contributions due to vibrational averaging. See ref 55 for a detailed treatment.

Similarly we have, using the Lorenz−Lorentz equation[53] and a quartic extrapolation of the refractive data,[56,57] estimated the frequency-dependence of the polarizability of liquid water to be given by the expression $\alpha_{liq}^{exp}(\omega) = 9.625 + 60.27\omega^2 - 1124.4\omega^4$. This gives a reasonable fit to the results derived from the Lorenz−Lorentz equation for frequencies in the range from 0.04 au to 0.12 au. We note that the approximate Lorenz−Lorentz equation really applies to the gas phase but is here (as many other places) used in the context of liquid, which may be considered somewhat troublesome. Therefore, deviations between the experimental Lorenz−Lorentz derived liquid polarizabilities and the CC/MM predictions are expected. From this expression we observe that at small frequencies the polarizability is decreased when going from gas phase to the liquid phase. For an example we find from this expression that $\alpha_{liq}^{exp}(0.0428) = 9.73$ au, and as the polarizability is increased as a function of the frequency in the gas phase the polarizability in the gas phase is somewhere between 9.83 au and 9.92 au which is larger than 9.73 au. This observation is not in agreement with the CC/MM results where $\bar{\alpha}$ is increased when going from vacuum to liquid phase. This is also observed using the DRF/DFT[27] and MCSCF/MM[17] methods. At larger frequencies the experimental polarizability of the liquid becomes larger than the gas-phase polarizability as the dispersion of the liquid polarizability is more significant compared to the gas-phase polarizability. This is not observed using neither CC2 or CCSD (see Table 4) nor DFT[27] or MCSCF[17] where the frequency dependence in a vacuum and the liquid phase is found to be almost identical.

To compare the absolute value of the polarizability using the CC/MM methods with the experimentally values we have to account for the vibrational contributions to the polarizability. As the pure vibrational (PV) contribution is minor at normal optical frequencies[58] we neglect this and only account for the zero point vibrational average (ZPVA) contribution to the polarizability. Reis et al. have calculated $\alpha^{ZPVA}(0.00) = 0.292$ au[59] at the MP2 level of theory. Assuming a similar dispersion as the electronic contribution we add this to the *A* values in Table 4 before calculating the polarizability at a given frequency. In this way we obtain $\bar{\alpha}_{liq}^{theory}(0.0856) = 10.5-10.6$ au from the CCSD/MM models and $\bar{\alpha}_{liq}^{theory}(0.0856) = 11.0-11.4$ au from the CC2/MM models which is to be compared to the experimental value of $\alpha_{liq}^{exp} = 10.01$ au. Again the agreement with the results derived from experiments through the Lorenz−Lorentz equation is not very good, in contrast to the good agreement between theory and experiment for the gas phase results. Obviously, the comparison of a bulk property like a polarizability with atomistic calculations will be troublesome and indirect. Certainly the use of the Lorenz−Lorentz equation to estimate the polarizability of individual water molecules from liquid-phase experiments is a crude approximation. On the side of the CC/MM calculations the use of a single average water structure to calculate the statistical average of the polarizability may be a significant approximation. Contributions from intra- and intermolecular vibrational degrees of freedom have not been addressed, and even at optical frequencies some contributions could still remain. In addition we have used the vacuum geometry of water in the liquid-phase calculation and the relaxation effects of the solvent on the geometry have therefore not been accounted for either.

V. Summary

In this paper we have presented linear response properties and excitation energies of liquid water calculated using different molecular mechanics approaches within coupled cluster theory.

We have compared the results obtained with the computational cheaper CC2 model with the CCSD model within the different solvent methods.

First, we have discussed how to obtain high quality MM parameters (partial charges and isotropic polarizability) which are determined by an iterative self-consistent procedure from the solvated QM system. The parameters are only dependent on the MM medium through the geometry of the MM system and the way the QM/MM interactions are defined. We have compared the results obtained using the optimized set of coupled cluster/molecular mechanics parameters to previous results. We find the set of parameters obtained from the coupled cluster/molecular mechanics iterative procedure to give results of the same quality as the previous calculated results.

Second, we have discussed how to minimize the computational costs of the coupled cluster/molecular mechanics model. We find that including a polarized solvent within a given radius of the QM system and the rest of the solvent only through point charges the results of a fully polarized solvent model is reproduced. However, this is done at a much lower computational cost as the point charges enter the CC/MM optimization conditions in a nonexpensive way in contrast to the polarizabilities. This encourages the introduction of an automatic screening of the polarization contributions in the CC/MM optimization conditions.

Generally, we find that the CC2/MM response properties and excitation energies deviate somewhat from the corresponding CCSD/MM results. However, the CC2/MM results show the same trends as the CCSD/MM results unlike some other QM/MM methods. Therefore, for investigations concerning larger QM systems the CC2/MM method may be preferred where MCSCF/MM is unable to account for the dynamical correlation, and DFT/MM may be subject to certain problems as discussed here in the case of excitation energies. Indeed CC2 has recently been cast in a new efficient approximate formulation applicable to large molecules.[62]

We find that in order to reduce the computational time but maintaining the quality of the results the combination of polarized solvent and nonpolarized solvent is preferred together with the CCSD/MM method as the quality of the results is essentially unchanged. We note that this approach in combination with the CC2/MM method provides an even faster option.

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(63) Here, d is short for double as the aug-cc-pVTZ [5s4p3d2f] basis set has been augmented with an extra set of diffusion s, p, d, and f functions analog to the way the aug-cc-pVTZ basis set was constructed from the cc-pVTZ [4s3p2d1f] basis set.[41] The exponents of the additional gaussians are constructed in an even-tempered way using $\zeta_i = \alpha\beta^{i-1}$.