Application of a Drude model to the binding of excess electrons to water clusters

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A one-electron model potential approach for calculating the binding energies of an excess electron interacting with water clusters is presented. Drude oscillators are employed on the water monomers to describe electron–water polarization and dispersion interactions. It is demonstrated that the resulting model gives electron binding energies very close to the predictions of *ab initio* CCSD(T) calculations. Dispersion interactions and high-order renormalization effects are found to make large contributions to the electron binding energies. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Negatively charged water clusters have long held a special fascination for physicists and chemists, and despite numerous experimental[1–9] and theoretical studies,[9–13] there remain significant gaps in our understanding of these species. Among the many outstanding questions are the following: (1) What is the minimum size cluster for which the excess electron ''prefers'' interior binding rather than surface binding? (2) How are the $(H_2O)_n^-$ ions formed in the various experimental studies? (3) What is the origin of the magic numbers in the mass spectral distributions observed experimentally? (4) What are the geometries of the $(H_2O)_n^-$ ions responsible for the IR spectra measured by Ayotte *et al.*[5]?

It is now well established that using *ab initio* methods the accurate prediction of the binding of excess electrons to clusters of polar molecules requires the use of very flexible basis sets and inclusion of electron correlation effects,[14–19] preferably at the CCSD(T),[20] and in some cases,[21] even the CCSDT level of theory. However, even for a cluster as small as $(H_2O)_4^-$ single-point CCSD(T) calculations using a large basis set requires on the order of three days CPU time on a modern workstation. This precludes the use of accurate *ab initio* methods for optimizing geometries, calculating vibrational spectra, and for carrying out studies of the dynamics for any but the smallest clusters [e.g., $(H_2O)_2^-$ and $(H_2O)_3^-$].

In this study, we consider an alternative approach, namely the use of a one-electron model potential for describing the excess electron–water cluster systems. The motivation for a model potential approach comes from the realization that the excess electron occupies an extended orbital with very little charge density in the valance region of the water monomers. Indeed, several groups have introduced such model potentials for studying the interactions of excess electrons with water clusters and bulk water.[19–32] Generally, the model potential approaches couple a water–water model potential with terms to account for the interaction of an excess electron with the water molecules. Although the studies using such model potentials have provided valuable insights into excess electron–water systems, they suffer from two shortcomings: (1) the water–water potentials used generally do not provide a realistic description of the potential energy surfaces of the neutral water clusters, and (2) dispersion interactions between the excess electron and the water monomers have been neglected. The latter shortcoming is of particular concern as it is now well documented that such dispersion interactions can significantly enhance the electron binding.[10,14–19,33]

In this work, the Dang–Chang (DC) polarizable model for water,[32] which has been found to do a good job at describing small water clusters and bulk water,[32,34] is combined with a recently introduced model[33] for describing the electron–molecule interactions. The unique feature of the latter model is the use of Drude oscillators[35] to treat electron–water monomer polarization and dispersion. The resulting one-electron model potential approach is applied to $(H_2O)_3^-$ and $(H_2O)_4^-$, and the results are compared with the predictions of *ab initio* CCSD(T) calculations. The computational details are described in Sec. II, with the results being presented in Sec. III, followed by Discussion and Conclusions sections.

II. COMPUTATIONAL METHODOLOGY

A. Model potential

The DC water model employs the experimental geometry of the gas phase monomer (ROH=0.9572 Å, HOH angle=104.52°) and is a rigid-monomer model. Point charges are located at the positions of the H atoms (Q =0.519e) and on the rotational axis, displaced 0.215 Å from the O atom (towards the H atoms) (Q=−1.038e). This gives a dipole moment of 1.848 D, nearly identical to the experimental value of 1.825 D[36] and quadruple moment components of Q_{xx}=2.235 D·Å, Q_{yy}=−2.047 D·Å, and Q_{zz}=−0.188 D·Å in fairly good agreement with experiment values of Q_{xx}=2.626 D·Å, Q_{yy}=−2.493 D·Å, and Q_{zz}=−0.134 D·Å.[37] The DC model also locates a polarizable center at the same position as the negative charge. The

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polarizability is taken to be isotropic, with the numerical value of 1.444 Å^3, chosen to match the experiment.[38] Finally; a single Lennard-Jones site is centered on the O atom ($\epsilon = 0.1825$ kcal/mol, $\sigma = 3.2340$ Å).

The water–water interactions thus include electrostatic (charge–charge), charge-induced dipole, and Lennard-Jones type interactions. The induced dipoles on the different monomers are allowed to interact, and the polarization equations giving the net induced dipole moments are solved self consistently.

The Hamiltonian (in atomic units) for an excess electron interacting with a single water molecule and neglecting polarization and dispersion is taken to be

$$H_{DC}^{el} = -\frac{1}{2}\nabla^2 - \sum_j \frac{Q_j}{r_j} + V^{ex} + V^{rep}, \tag{1}$$

where the sum is over the charge sites of the monomer, and V^{ex} and V^{rep} represent the exchange and electron–molecule repulsive interactions, respectively. The subscript ''DC'' implies that the charges and their locations are from the DC model. As will be discussed below, we also consider a second model based on Hartree Fock (HF) charges in which case the electronic Hamiltonian is designated H_{HF}^{el}. V^{rep} is generated following the procedure of Schnitker and Rossky,[22] except that we represent it in terms of Gaussian instead of Slater functions.[33] Also, following Schnitker and Rossky, V^{ex} is ignored as it is expected to be relatively unimportant for the electron binding to water clusters.

Electron–molecule polarization and dispersion are accounted for by associating with the monomer a Drude oscillator[35] consisting of two charges $+q$, $-q$, separated by a distance R and coupled harmonically through the force constant k. The reduced mass of the oscillator is m_0. The Drude oscillator is located at the same position as the polarizable center in the DC model. This results in a coupling term of the form

$$V^{couple} = \frac{q\mathbf{r}\cdot\mathbf{R}}{r^3}\cdot(1 - e^{-br^2}), \tag{2}$$

where $\mathbf{r}$ is the position of the electron relative to the oscillator, and $(1 - e^{-br^2})$ is a damping factor, which attenuates unphysical short-range interactions between the excess electron and the Drude oscillator. The total Hamiltonian then becomes

$$H = H^{el} + H^{osc} + V^{couple}. \tag{3}$$

Both the Drude oscillator and the excess electron are treated quantum mechanically using a product basis set of the form $|\phi_\beta\chi_i\rangle$ where ϕ_β and χ_i are eigenfunctions of H^{el} and H^{osc}, respectively. The electron binding energy for the full model Hamiltonian is calculated using the second-order perturbation theory and the configuration interaction (CI) methods. In addition, electron binding energies are also calculated using H^{el} alone, i.e., neglecting coupling to the Drude oscillators. The latter binding energies are referred to as Koopmans' theorem (KT)[39] values, since they result from a static approximation neglecting polarization and dispersion.

As shown in Ref. 33, the second-order correction to the electron binding energy for the model Hamiltonian system can be decomposed into polarization and dispersion contributions. The former is proportional to q^2/k, which is simply the polarizability of the Drude oscillator, here set equal to either the HF or DC polarizability values of a water monomer. (Anisotropic polarizabilities can be accounted for by introducing separate k_x, k_y, and k_z force constants.) The second-order dispersion contribution is

$$\epsilon^{disp} = \sum_s \sum_{\beta\neq 0} \frac{\frac{q^2}{2k}\left|\left\langle 0\left|\frac{s}{r^3}\right|\beta\right\rangle\right|^2}{-1 + (\epsilon_0 - \epsilon_\beta)\sqrt{\frac{m_0}{k}}}, \tag{4}$$

where the first summation runs over $s = x$, y, and z, and the second runs over the excited electronic levels.[33] However, since the excess electron is weakly bound, the sum over β is dominated by terms for which $|(\epsilon_0 - \epsilon_\beta)\sqrt{m_0/k}| \ll 1$, the dependence on m_0 should be quite weak. In this work, m_0 is taken to be the mass of an electron, and q is taken to be 1. Note that if the excess electron were highly localized, Eq. (4) would reduce to the London expression for dispersion.

The extension of the Drude model to a cluster of molecules is straightforward. The Hamiltonian for the excess electron now includes electrostatic and repulsive interactions with each monomer, as well as interactions with a Drude oscillator on each molecule. The basis set for an electron interacting with n Drude oscillators consists of functions of the form $|\phi_\alpha\chi_l^{(1)}\cdots\chi_m^{(n)}\rangle$ where ϕ_α is again an electron orbital and χ_l^j is the lth level associated with the jth oscillator.

Intermolecular induction and polarization can be treated either through the standard approach for the DC model or *via* coupling between the Drude oscillators. The latter approach has the advantage of including, in a self-consistent manner, three- and higher-body induction and dispersion effects, both among the monomers as well as in the electron and monomer interactions. In the present study, we adopt an intermediate approach, in which the induction is treated using Drude oscillators but the intermolecular dispersion is accounted for *via* the Lennard-Jones terms in the DC water model. This decouples electron–molecule and molecule–molecule dispersion, which should be a good approximation as three-body dispersion effects are expected to be relatively unimportant for water clusters.

In applying the model Hamiltonian approach to clusters, we incorporate into the zeroth-order electronic Hamiltonian the interaction of the excess electron with the induced dipoles on the monomers.[33] That is, the zeroth-order energy levels of the excess electron are calculated in the field of the charges plus the induced dipole moments.

The electronic basis set is chosen to consist of even-tempered series of s and p primitive Gaussian-type functions, the number and exponents of which depend on the cluster being treated. Additional details are provided below after the specific water clusters to be studied are introduced. A basis set of the form (ψ_l, ψ_m, ψ_n), $0 \leq l + m + n \leq 2$, where l, m, and n are quantum numbers associated with a three-

dimensional harmonic oscillator in Cartesian representation, is employed on each Drude oscillator. Test calculations show that this oscillator basis set is adequate for describing electron–water polarization and dispersion as well as inter-molecular induction.

Although the ultimate goal of the model potential calculations is to provide a quantitatively correct description of electron binding to water clusters, it is important to check that the model employed correctly describes electron binding in the absence of electron–water polarization and dispersion. However, one cannot simply compare the electron binding energies calculated using H_{DC}^{el}, described above, with *ab initio* Koopmans' therorem (KT) binding energies. The reason for this is that H_{DC}^{el} employs charges that give the correct dipole moment and realistic quadruple moment components, whereas *ab initio* KT binding energies are obtained using the Hartree–Fock (HF) procedure, which considerably overestimates the dipole moment for the water monomer. Thus to facilitate comparison, we have also carried out model potential calculations with H_{HF}^{el}, in which the DC charges are replaced by charges determined from Hartree–Fock electrostatic potential calculations on the water monomer. Intramolecular polarization is included by choosing q^2/k to reproduce the Hartree–Fock polarizability of a water monomer and allowing the permanent charges in the H_{HF}^{el} model to interact with the Drude oscillators.

In our earlier work on $(HCN)_n^-$ and $(HNC)_n^-$, $n=1, 2$, it was found that the one-electron model, with charges and polarizabilities from Hartree–Fock calculations, and with the repulsive potential derived using the procedure described in Ref. 22, gave electron binding energies considerably lower in magnitude than the *ab initio* KT values.[33] This was primarily a consequence of the approximations used in the generation of the repulsive core. This problem was solved by rescaling the repulsive potential so that the electron binding energies for the HCN and HNC monomers calculated using the model potential procedure reproduced the *ab initio* KT binding energies. The scaling factors obtained for the monomers also proved satisfactory for the dimers. Moreover, with this rescaling, the model potential method including coupling between the excess electrons and the Drude oscillators was found to give polarization and dispersion contributions to the electron binding energies close to the *ab initio* results.

For water clusters, it is necessary to modify this strategy somewhat because the monomer does not bind an electron. (Actually, in the Born–Oppenheimer approximation, a water monomer does weakly bind an electron. However, were corrections to the Born–Oppenheimer approximation made, the excess electron would no longer bind.) For that reason, we have used the water dimer, which does have a bound anion state, to determine the scaling factor for the repulsive potential. This scaling factor is used in all subsequent calculations of electron–water interactions, including those discussed below based on the model potential employing DC charges and polarizability values.

The calculations on the water dimer were also used to determine the value of b in the factor damping the coupling

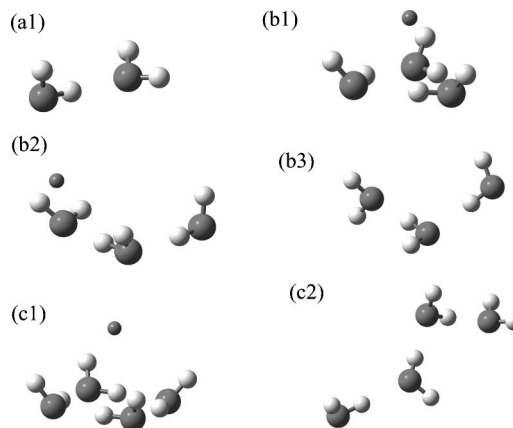FIG. 1. MP2 optimized geometries of the $(H_2O)_n^-$, $n=2-4$ clusters: (a1) $(H_2O)_2^-$, crown (b1), transition state (b2), and chain (b3) structures of $(H_2O)_3^-$, crown (c1) and chain (c2) forms of $(H_2O)_4$. For the crown and transition state structures, the small black dot indicates the center of the extended set of diffuse basis functions.

of the electron to the Drude oscillators. Specifically, b was chosen so that the model potential CI binding energy reproduced the *ab initio* CCSD(T) result. This gave a b value of 0.43.

B. Details of $(H_2O)_3^-$ and $(H_2O)_4^-$ calculations

In this work, we consider both chain-like and cyclic crown-like local minima of the $(H_2O)_3^-$ and $(H_2O)_4^-$ clusters (see Fig. 1). In the crown-like structures, the free OH groups all point in the same direction. The neutral $(H_2O)_3$ and $(H_2O)_4$ clusters, at the optimized structures of the anions, have large dipole moments, and thus the excess electron can be viewed as being dipole-bound.[14–16,40,41] Interestingly, for the neutral clusters, neither the chain-like nor the crown-like structures are potential energy minima. Thus the binding of the excess electron overcomes the tendency of these neutral clusters to rearrange. For $(H_2O)_3^-$ we also present results for the transition state for interconversion of the chain-like and crown-like structures.[42]

We now turn to the electronic basis sets used in the model potential and *ab initio* calculations. In the model potential calculations, the basis set consisted of two s Gaussian functions with exponents 0.02526 and 0.1027 and two p functions with exponents 0.141 and 0.727 on each H atom[43] together with a large set of diffuse s and p Gaussian functions on the O atom on the terminal water (at the +dipole end) in the chain-like structures and on the rotational axis for the crown-like clusters. In the latter case the displacement of the center of the diffuse functions from the plane of the O atoms was optimized so as to maximize the electron binding energies. For the model potential calculations on $(H_2O)_3^-$, the large, single-center portion of the basis set was chosen to consist of an even-tempered series of six s and five p functions. For the calculations on the crown-like structure of $(H_2O)_4^-$, five s and four p functions were used, whereas for the linear form of $(H_2O)_4^-$, four s and three p functions were used. (For species with a large dipole moment, the dipole

TABLE I. Diffuse Gaussian functions used in calculations on the $(H_2O)_n^-$ clusters.

$(H_2O)_2^-$		$(H_2O)_3^-$		Crown $(H_2O)_4^-$		Chain $(H_2O)_4^-$	
s	p	s	p	s	p	s	p
2.5×10^{-2}	6.0×10^{-2}	7.5×10^{-2}	6.0×10^{-2}	3.0×10^{-2}	3.0×10^{-2}	3.0×10^{-2}	3.0×10^{-2}
5.0×10^{-3}	1.2×10^{-2}	1.5×10^{-2}	1.2×10^{-2}	6.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}
1.0×10^{-3}	2.4×10^{-3}	3.0×10^{-3}	2.4×10^{-3}	1.2×10^{-3}	1.2×10^{-3}	1.2×10^{-3}	1.2×10^{-3}
2.0×10^{-4}	4.8×10^{-4}	6.0×10^{-4}	4.8×10^{-4}	2.4×10^{-4}	2.4×10^{-4}	2.4×10^{-4}	
4.0×10^{-5}	9.6×10^{-5}	1.2×10^{-4}	9.6×10^{-5}	4.8×10^{-5}			
		2.4×10^{-5}					

bound electron is more localized, and a smaller basis set can be employed.) The exponents of the basis functions are listed in Table I. Test calculations revealed that the adoption of still more flexible basis sets had very little effect on the electron binding energies.

The *ab initio* calculations employed a flexible basis set suitable for describing the neutral water molecules together with the same single-center sets of diffuse s and p functions as used for the model potential calculations. A $(11s6p2d/6s2p)\rightarrow[5s4p2d/4s2p]$ basis set was first adopted for the water molecules. (The uncontracted basis set is given in parentheses and the contracted set in brackets. The O atom basis set is specified first, followed by the H atom basis set.) For the O atoms, the s and p functions were taken from the aug-cc-pVTZ basis set and the d functions from the aug-cc-pVDZ basis set.[44] Similarly for the H atoms, the basis set was formed by combining the s functions from the aug-cc-pVTZ basis set with the p functions from the aug-cc-pVDZ basis set. This mixed basis set was found to give at the MP2 level a dipole moment and polarizability of the water monomer close to the corresponding experimental values, while being less computationally demanding than the full aug-cc-pVTZ basis set.

Ab initio results are reported at the KT, MP2, and CCSD(T) levels of theories. For the last two methods the electron binding energies are obtained by subtracting the energy of the neutral from that of the anion at the specified level of theory. The second-order contributions to the electron binding energies are divided into dispersion and nondispersion components using the procedure of Gutowski *et al.*[16,17] This procedure associates the dispersion contribution with those terms in the expression for the second-order correlation energy of the anion that involve simultaneous excitations from the dipole-bound orbital and one of the occupied orbitals of the water cluster.

To facilitate comparison of the model potential and *ab initio* results, the same geometries were used for the two sets of calculations. The geometries of the anions were optimized at the *ab initio* MP2 level of theory under the constraint of rigid monomers, using the OH bond length and HOH angle values employed in the DC model. These geometries were then used for the *ab initio* calculations on the neutral and anionic species and for the model potential calculations on the anions.

III. RESULTS

A. $(H_2O)_2$

Table II summarizes the results for $(H_2O)_2$. By construction, the KT binding energy from the model potential employing the HF charges and polarizabilities, (model I) matches the *ab initio* KT value of 11.1 meV, and the CI binding energy from the model based on H_{DC}^{el} (model II) reproduces the *ab initio* CCSD(T) binding energy of 33.0 meV. Experimental estimates of the vertical detachment energy of $(H_2O)_2^-$ are 30 ± 4 meV and 45 ± 6 meV.[45,46]

It should be noted that the DC model tends to underestimate the induced dipole moments of water clusters. For example, for the dimer, with the geometry employed here, the DC model gives a net dipole moment of 4.02 D, compared with the dipole moment of 4.13 D obtained from *ab initio* MP2 calculations; for the chain-like form of the tetramer, the discrepancy is 0.29 D. In general, the underestimation of the dipole moments would be expected to lead to an underestimation of the electron binding energies. However, by choosing the scaling factor of the repulsive potential

TABLE II. Electron binding energies (meV) for the water dimer.[a]

Method	Energy contribution				
	KT	Polariz.	Disp.	MP2[b]	CCSD(T)/CI[c]
Ab initio	11.1	0.6	12.0	19.7	33.0
Model I	11.1	0.6	11.1	22.8	40.0
Model II	6.4	0.3	7.9	14.7	33.0

[a]Scaling factor 6.8, damping factor $b=0.43$.
[b]MP2 denotes the electron binding energies calculated through second order, and which sums the KT, polarization (Polariz.), second-order dispersion (Disp.), second-order nondispersion contributions.
[c]This column reports electron binding energies obtained from *ab initio* CCSD(T) and model-potential CI calculations.

TABLE III. Electron binding energies (meV) of the water trimer.

Structure	Method	Energy contribution				
		KT	Polariz.	Disp.	MP2[a]	CCSD(T)/CI[b]
Crown	*Ab initio*	3.3	0.1	4.0	5.7	13.0
	Model I	3.3	0.1	3.9	7.3	17.4
	Model II	1.4	0.1	2.2	3.7	13.6
Transition	*Ab initio*	34.8	3.3	31.6	59.8	87.0
state	Model I	34.8	3.0	28.7	66.6	101.7
	Model II	23.2	2.1	23.6	48.9	89.5
Chain	*Ab initio*	60.7	4.4	43.8	97.1	127.0
	Model I	60.4	4.3	40.6	105.3	142.1
	Model II	45.0	3.5	36.5	85.0	128.6

[a]MP2 denotes the electron binding energies calculated through second order, and which sums the KT, polarization (Polariz.), second-order dispersion (Disp.), second-order nondispersion contributions.
[b]This column reports electron binding energies obtained from *ab initio* CCSD(T) and model-potential CI calculations.

so that the KT calculations using model I reproduce the *ab initio* KT electron binding energy and the damping factor *b* so that the CI calculations using model II reproduce the *ab initio* CCSD(T) electron binding energy of the water dimer, we partially correct for this shortcoming of the DC model.

B. $(H_2O)_3^-$

Table III reports for $(H_2O)_3^-$ the electron binding energies obtained using models I and II and from the *ab initio* calculations. We consider first the results of the *ab initio* calculations. In the KT approximation the excess electron is bound by 3.3 and 66.7 meV in the crown-like and chain-like forms of $(H_2O)_3$, respectively. The corresponding binding energies obtained from the CCSD(T) calculations are 13.0 and 127.0 meV. The MP2 binding energies are roughly intermediate between the KT and CCSD(T) values. As has been found for other dipole-bound anions, polarization (estimated by the difference between the KT and ΔSCF binding energies) makes relatively small contributions to the electron binding energies.[14,33] The decomposition procedure of Gutowski *et al.* gives second-order dispersion contributions to the electron binding energies of 4.0 and 43.8 meV for the crown-like and chain-like forms of $(H_2O)_3$, respectively. These dispersion contributions are roughly comparable to the KT binding energies. The nondispersion contributions to the electron binding energies act so as to reduce the binding energies by 1.7 and 11.8 meV for the crown- and chain-like structures, respectively. This is primarily a consequence of the reduction of the monomer dipole moments brought about by the inclusion of electron correlation effects.

The one-electron model-potential approach employing HF charges and the HF polarizability for the monomers (model I) gives KT binding energies very close to the corresponding *ab initio* values. The polarization and dispersion contributions calculated using model I are also in excellent agreement with the *ab initio* results.

The net electron binding energies calculated through second-order using model I are considerably (8–34%) larger than the *ab initio* MP2 results. This is largely due to the use of HF atomic charges in model I, whereas the *ab initio* MP2 calculations build in a charge renormalization, which causes a reduction of the dipole moments of the water monomers.

We now examine the results obtained using the one-electron model potential with the DC charges and polarizability (model II). Most significantly, model II gives electron binding energies at the CI level very close to the *ab initio* CCSD(T) results. For the chain-like form of $(H_2O)_3^-$, the *ab initio* CCSD(T) and model potential calculations give electron binding energies of 127.0 and 128.6 meV, respectively. The corresponding results for the crown-like form of $(H_2O)_3^-$ are 13.0 and 13.6 meV. The experimental value of the vertical electron detachment energy of $(H_2O)_3^-$ (presumably with a chain-like geometry) is 150 ± 15 meV,[8] which is somewhat larger than the model potential CI and *ab initio* CCSD(T) values for the chain-like form of the anion. This discrepancy is primarily a consequence of our use of rigid-monomers in both the model potential and *ab initio* calculations, which leads to an underestimation of the dipole moment of the neutral molecule.

Table III also reports results for the transition state for interconversion of the crown-like and chain-like isomers of $(H_2O)_3^-$. The electron binding energy for this transition state is intermediate between that of the two minimum energy structures. This is consistent with the trends in the dipole moments of the corresponding neutral clusters. Again there is excellent agreement between the electron binding energy from model II CI calculations and that from the *ab initio* CCSD(T) calculations.

C. $(H_2O)_4^-$

The excess electron is bound much more strongly in the $(H_2O)_4^-$ isomers than in their $(H_2O)_3^-$ counterparts, consistent with the larger dipole moments for the neutral $(H_2O)_4$ than $(H_2O)_3$ clusters. At the *ab initio* KT level, the crown- and chain-like forms of $(H_2O)_4^-$ are bound by 12.5 and 110.2 meV, respectively (see Table IV). The corresponding values at the MP2 level are 20.9 and 170.3 meV, and at the CCSD(T) level, they are 36.5 and 209.7 meV. The decomposition procedure of Gutowski *et al.* again reveals that there are large dispersion and nondispersion contributions to the
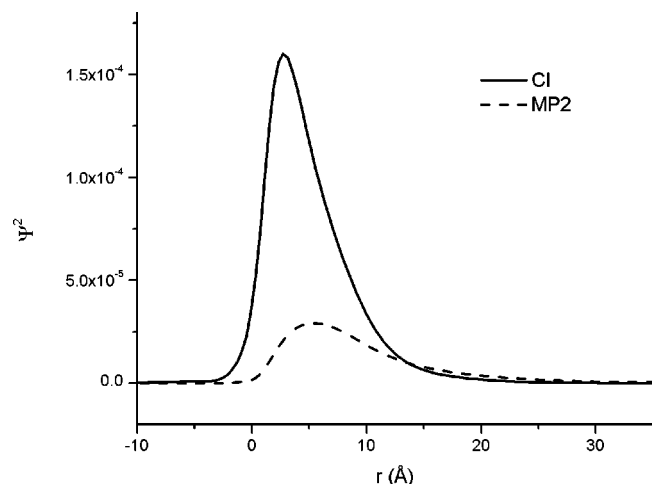
FIG. 2. Plot of the electron density of the crown-like form of $(H_2O)_4^-$ calculated using the CI (solid line) and MP2 (dashed line) methods in conjunction with model II. The density is plotted along the C_4 axis, with the origin being located in the plane of the four O atoms. (The free OH hydrogen atoms are located 0.75 Å above the O-atom plane.)

FIG. 4. Plot of the electron density of the crown-like form of $(H_2O)_4^-$ calculated using the CI (solid line) and MP2 (dashed line) methods in conjunction with model II and model III, respectively. Model III is identical to model II except that the charges have been adjusted to reproduce the binding energy obtained from the model II CI calculations. The density is plotted along the C_4 axis, with the origin being located in the plane of the four O atoms.

electron binding energies which act in opposite directions. However, because the dispersion contributions are larger in magnitude, there is a net enhancement of the electron binding energies upon the inclusion of second-order correlation effects.

Model I gives KT binding energies and second-order dispersion contributions to the binding energies close to the *ab initio* results. As expected, MP2 calculations with model I overestimate the electron binding energies as compared to the *ab initio* MP2 results.

The CI calculations with model II give electron binding energies for the crown-like and chain-like forms of $(H_2O)_4^-$ very close to the *ab initio* CCSD(T) values. Specifically the model potential calculations give electron binding energies of 40.0 and 212.5 meV for the crown-like and chain-like isomers, respectively, whereas the corresponding *ab initio*
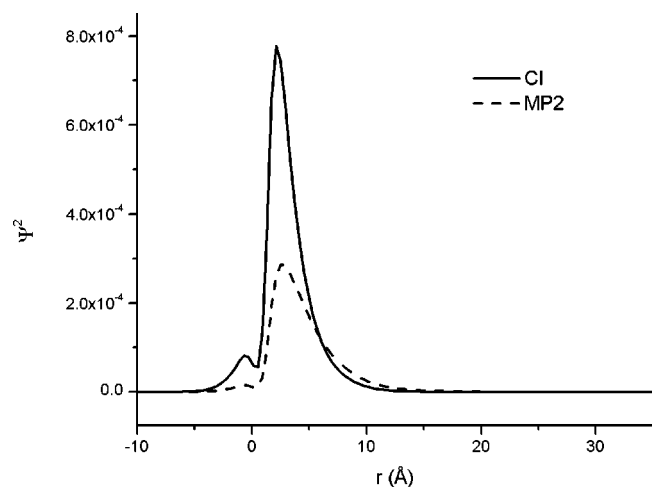
CCSD(T) values are 36.5 and 209.7 meV. The agreement is better than might have been expected, especially for the chain-like structure, given the considerable (≈ 0.29 D) underestimation of the net dipole moment of the neutral cluster by the DC model. It may be that the error due to the underestimation of the dipole moment is offset by slightly too weak a damping of the coupling of the electron to the Drude oscillator.

We are unaware of any experimental measurement of the vertical detachment energy for the chain-like form of $(H_2O)_4^-$. However, we anticipate that the present calculations [both CCSD(T) *ab initio* and CI model potential] give electron binding energies 10–20% smaller than the "true" value due to the use of rigid monomer approximation.

FIG. 3. Plot of the electron density of the chain-like form of $(H_2O)_4^-$ calculated using the CI (solid line) and MP2 (dashed line) methods in conjunction with model II. The plot is along the direction of the dipole of the water chain. The origin is taken to coincide with the O atom of the terminal acceptor water molecule.
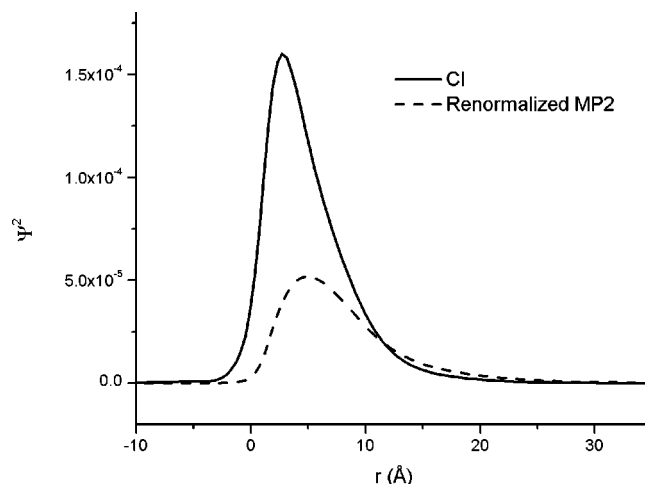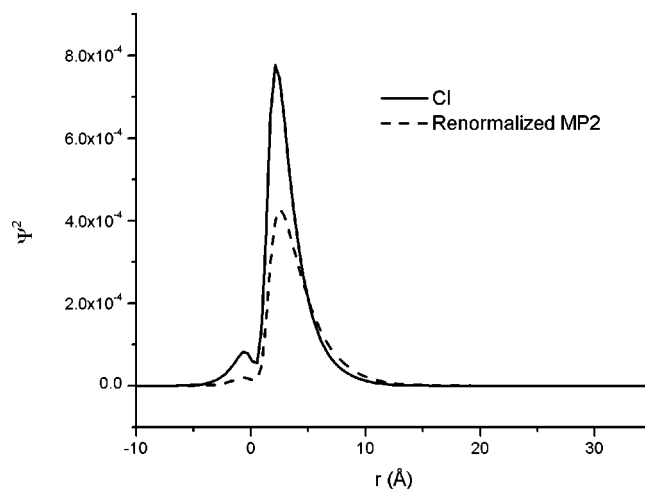

FIG. 5. Plot of the electron density of the chain-like form of $(H_2O)_4^-$ calculated using the CI (solid line) and MP2 (dashed line) methods in conjunction with model II and model III, respectively. Model III is identical to model II except that the charges have been adjusted to reproduce the binding energy obtained from the model II CI calculations. The plot is along the direction of the dipole of the water chain. The origin is taken to coincide with the O atom of the terminal acceptor water molecule.

TABLE IV. Electron binding energies (meV) of the water tetramer.

Structure	Method	Energy contribution				
		KT	Polariz.	Disp.	MP2[a]	CCSD(T)/CI[b]
Crown	*Ab initio*	12.5	0.8	12.1	20.9	36.5
	Model I	12.9	0.9	11.7	25.6	46.6
	Model II	7.3	0.5	8.5	16.3	40.0
Chain	*Ab initio*	110.2	8.2	67.7	170.3	209.6
	Model I	109.2	8.1	62.6	179.9	227.2
	Model II	87.8	7.3	59.7	154.7	212.5

[a]MP2 denotes the electron binding energies calculated through second order, and which sums the KT, polarization (Polariz.), second-order dispersion (Disp.), second-order nondispersion contributions.
[b]This column reports electron binding energies obtained from *ab initio* CCSD(T) and model-potential CI calculations.

D. Electron densities and importance of single excitations

Figure 2 reports the charge distribution of the crown-like form of $(H_2O)_4^-$ obtained using the MP2 and CI methods in conjunction with model II. The charge distribution obtained in the KT approximation and using model II is nearly identical to that obtained using the MP2 method, and thus has not been plotted. The similar charge densities obtained from the KT and MP2 approximations is somewhat surprising given the sizable enhancement in electron binding energy in going from the KT to the MP2 approximation. However, this is consistent with the observation that the wavefunction through first order is dominated by the reference configuration, the coefficient of which is 0.998 in the normalized wavefunction. Hence, even though dispersion interactions make a sizable contribution to the electron binding energy, they have very little impact on the distribution of the excess electron.

In contrast to the relative insensitivity of the distribution of the excess electron to first-order corrections to the wavefunction, there is a large difference between the charge distributions obtained from the MP2 and full CI model potential calculations, with the charge distribution associated with the full CI wavefunction being much more localized. The coefficient of the reference configuration in the CI wavefunction for the crown-like form of $(H_2O)_4^-$ is only 0.82.

The large change in the wavefunction (and in the electron binding energy) in going from the MP2 to the CI method is due primarily to configurations in which the electron is excited but the Drude oscillators are unexcited. In a perturbative treatment, these single excitations first enter the wavefunction in second order and the energy in fourth order, and they be thought of as a renormalization in response to the dispersion interactions. The reason that these single excitations prove so important is apparent from examination of the perturbative expressions, from which it is seen that they enter with factors of $\epsilon_0 - \epsilon_j$ or $\epsilon_i - \epsilon_j$, where ϵ_0 and ϵ_j are energies associated with H^{el}, in the energy denominators. In contrast, the terms involving excitation of both the electron and a Drude oscillator involve factors in the denominator of the form $\epsilon_0 - \epsilon_j + \epsilon_D$, where ϵ_D is the energy spacing between levels of the Drude oscillator. Since the energy levels of the excess electron are closely spaced compared to those of the Drude oscillator, configurations in which the electron is excited but the Drude oscillators are unexcited lead to sizable corrections to the wavefunction and the electron binding energy. The sizable high-order corrections to the electron binding energies of dipole-based anions found in all-electron *ab initio* calculations[14–18] have a similar origin, i.e., they arise from configurations, in which the excess electron is excited but the electrons of the molecule or cluster are unexcited.

Figure 3 displays the charge distribution of the excess electron of the chain-like form of $(H_2O)_4^-$ calculated using the MP2 and CI methods in conjunction with model II. As for the crown-like anion, the KT calculations using model II give nearly the same electron distribution as obtained from the MP2 calculations, whereas there is a considerable contraction of charge density upon the inclusion of configurations involving excitation of the electron only.

TABLE V. A comparison of electron binding energies (meV) from MP2 calculations with model III, CI calculations with model II, and *ab initio* calculations.

Methods	Energy contribution					
	$(H_2O)_2$ chain	$(H_2O)_3$ crown	$(H_2O)_3$ TS	$(H_2O)_3$ chain	$(H_2O)_4$ crown	$(H_2O)_4$ chain
Ab initio CCSD(T)	33.0	13.0	87.0	127.0	36.5	209.6
Model II CI	33.0	14.0	89.8	127.8	40.5	210.8
Model III MP2	34.8	10.5	91.9	142.5	33.7	236.5

E. Renormalized MP2-level model potential

Because our long-range goal is to apply the one-electron Drude model to describe electron binding to large water clusters, the computational speed of the calculations is of importance. This leads us to ask whether the MP2 method can be "renormalized" to give near CI quality results (see Table IV). Here we consider a crude renormalization in which the magnitudes of the permanent charges in model II have been scaled so that for $(H_2O)_2^-$ MP2 calculations approximately reproduce the electron binding energy from the *ab initio* CCSD(T) calculations. This renormalized model (hereafter designated as model III) underestimates the electron binding energies of the crown structures (by up to 20%) and overestimates the electron binding energies of the chain-like structures by up to 8% (see Table V). Moreover, it gives electron distributions that are too extended (i.e., diffuse), compared to those from the CI calculations and using model II (as seen from Figs. 4 and 5). Nonetheless, model III should be useful for qualitative (even semi-quantitative) prediction of the electron binding energies of large water clusters.

IV. DISCUSSION AND CONCLUSIONS

In the present study we show that the Dang–Chang water model, coupled with a one-electron model potential employing Drude oscillators to describe electron–molecule polarization and dispersion, is able to account in a near quantitative manner for the binding of an excess electron to small water clusters. Dispersion and high-order "renormalization" corrections lead to large enhancements of the electron binding energies compared to those predicted from a "purely" electrostatic model neglecting dispersion interactions. Configurations in which the excess electron is excited but the Drude oscillators are unexcited are found to cause sizable enhancements of the electron binding energies and significant contraction of the charge distributions of the excess electron. This contraction greatly increases the charge density near the H atoms near the end of the chains in the chain-like isomers and in the vicinity of the free OH groups in the crown-like isomers. This, in turn, should prove important for the intensities of the OH stretching vibrations in IR spectroscopy of the anion and also for the presence of the OH stretching vibrational structure in the detachment spectra.

For comparison with experimental electron detachment energies and for calculating vibrational spectra, it will be necessary to extend the present model to allow for flexible monomers. This flexibility is especially important for the electron binding energies as both the permanent and induced dipoles associated with the monomers change with distortions of the monomers.

Although the present investigation has focused on dipole-bound anions of water clusters, the Drude-model approach should also be applicable to a wide range of systems with weakly bound electrons. Extensions currently underway in our group include the development of Drude models for treating electron–inert gas interactions for the characterization of $(H_2O)_n^- Ar_m$ clusters and Xe_n^- clusters. Finally, we observe that the approach can also be combined with *ab*

initio methods to describe species such as $CH_3NO_2^-(H_2O)_n$, with the $CH_3NO_2^-$ ion being described within an all-electron framework and the water molecules by means of model potentials with Drude oscillators.

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