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A new electron-methanol molecule pseudopotential and its application for the solvated electron in methanol

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A new electron–methanol molecule pseudopotential is developed and tested in the present paper. The formal development of the potential is based on quantum mechanical calculations on the electron-methanol molecule model in the static exchange approximation. The computational model includes a steep confining potential that keeps the otherwise unbound excess electron in the vicinity of the methanol molecule. Using the Phillips-Kleinman theorem we introduce a smooth pseudo-wave function of the excess electron with the exact eigenenergy and correct asymptotic behavior. The non-local potential energy operator of the model Hamiltonian is then replaced to a local potential that reproduces the ground-state properties of the excess electron satisfactorily. The pseudopotential is then optimized in an analytically simple functional form to fit this approximate local potential in conjunction with the point charges and the geometry of a classical, all-site methanol-methanol interaction potential. Of the adjustable parameters, the parameters for the carbon and the methyl

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hydrogen atoms are optimized, while those for the oxygen and the hydroxyl hydrogen are taken from a previous electron-water molecule pseudopotential. A polarization term is added to the potential *a posteriori*. The polarization parameters are chosen to reproduce the experimental position of the optical absorption spectrum of an excess electron in mixed quantum-classical molecular dynamics simulations. The energetic, structural and spectroscopic properties of the solvated electron in a methanol bath are simulated at 300 K, and compared to previous solvated electron simulations and available experimental data.

I. Introduction

The physics of excess electrons in liquids have long been of interest in many diverse research areas. The hydrated electron, for example, plays a central role in various important physical processes in atmospheric chemistry, interstellar chemistry, and in electron-initiated processes in aqueous systems.¹ In a more general sense, the solvated excess electron may be thought of as a model system for solutions with a solute having a single electronic degree of freedom.

Besides the aqueous case, that has been the most extensively studied, experimental results for excess electrons in methanol are also available.^{2,3,4,5,6,7,8} Methanol, similarly to other polar solvents, localizes the excess electron in a solvent cavity surrounded by properly oriented methanol molecules. According to the ESR measurements of Kevan *et al.* on excess electrons in low-temperature methanol glass, the first solvation shell contains 4 ± 2 methanol molecules with an average hydroxyl hydrogen - electron distance of 2.3 ± 0.15 Å.³ The steady-state absorption spectrum of the solvated electron in methanol exhibits a broad, asymmetric band with a maximum at 1.95 eV.⁴ The advance of ultrafast laser techniques made it also possible to investigate the relaxation dynamics of the excess electrons in methanol on the sub-picosecond timescale.^{5,6} More recently, resonance Raman experiments of Mathies *et al.* provided the most complete picture of the solvation structure and dynamics of the solvated electrons in alcohols.⁷

As a relatively new development, recent years have witnessed a renowned interest, both experimental and theoretical, in studying finite size solvated electron systems, negatively charged solvent clusters. The interest is mainly motivated by the fact that cluster anions can facilitate the understanding of the transition from gaseous species to the bulk solvated electron. Despite the finite size and the anticipated relative simplicity of the cluster anions compared to bulk condensed phases, one faces serious difficulties in interpreting the

experimental observations, as clearly illustrated by the example of hydrated electron clusters.^{9,10,11,12,13,14,15} Up to now there is still no consensus on the most basic structural properties of water cluster anions. The most delicate unexplained problem is the appearance of at least three characteristic cluster anion classes reflected by three distinctly different trends in the variation of the vertical electron detachment energy with cluster size.¹⁴ A straightforward approach to solve the problematic issues is to extend the investigations to other polar solvents. The Neumark group has recently examined negatively charged methanol clusters by photoelectron imaging, and observed the signature of two different patterns of methanol cluster anions.⁸ The identification of these two methanol cluster anion classes is still to be resolved.

On the theoretical side, excess electrons have been studied in aqueous environment by both static quantum chemistry calculations,^{16,17} Car-Parrinello and Born-Oppenheimer quantum molecular dynamics simulations.^{18,19} The most extensive quantum chemistry calculations on excess electrons in methanol that we are aware of, have been performed using density functional methods using relatively modest basis sets.²⁰ The well-known problem is that all-electron (or, at least, all-valence-electron) quantum calculations are still expensive, and are limited to relatively small system size (i.e. few tens of atoms).

The mixed quantum-classical molecular dynamics (QCMD) technique offers an appealing simulation approach for examining the solvated electron system.^{21,22,23} The QCMD method replaces the quantum many-body problem to a one-electron problem in a bath of classically treated solvent molecules. The clear advantage of the QCMD method is that it allows relatively long simulation times for large systems. This approach has provided a reasonably simple framework to draw a consistent, in many cases semiquantitative, molecular level picture of the bulk hydrated electron.^{23,24,25,26,27,28,29,30} Despite the general agreement of experiment and theory, it has proved difficult to reproduce the position of the maximum and

the halfwidth of the optical absorption spectrum of the hydrated excess electron in bulk simulations.^{23,26,28} This serious deficiency clearly illustrated the importance of the proper choice of the electron-water molecule pseudopotential in QCMD simulations. The subsequent development of a new electron-water molecule pseudopotential,^{31,32} that reproduced the position of the optical absorption spectrum of the bulk hydrated electron, was the key element of a following series of QCMD simulations on hydrated electron clusters,^{33,34,35} excess electrons in bulk water³² and on water/air interfaces.³⁶ These simulations provided a detailed, molecular level picture on electron hydration, consistent with the experimental observations.^{10,11,14,15}

Up to now, of the two available electron-methanol molecule pseudopotentials,^{37,38} only one³⁷ has been used extensively in QCMD simulations. The structure, energetics and various dynamical aspects of an excess solvated electron in bulk methanol have been characterized in great detail.^{39,40,41,42,43,44} These examinations were also extended to metal/methanol surfaces.⁴⁵ Although the calculations provided a satisfactory picture of the bulk properties, the position of the absorption spectrum appears red-shifted in the simulations (1.72 eV vs 1.95 eV).³⁹ On the other hand, it would be desirable for the non-polarizable potentials to produce slightly blue-shifted spectra in order to compensate for the fact that the excited state energy is expected to decrease after proper self-consistent treatment of solvent electronic polarization in the presence of the excited electronic state. Similar arguments have been applied previously for the hydrated electron spectrum.³² An improved model of a solvated electron in methanol clearly requires a pseudopotential that reproduces the key energetic aspects of the absorption spectrum more precisely than the otherwise successful Zhu-Cukier potential.³⁷ Two additional points should also be mentioned. The Zhu-Cukier pseudopotential is based on the point charges, and the geometry of a three-site classical methanol model.³⁷ Application of an all-site classical methanol potential improves the atomistic character of the potential, and would

hopefully shed light on the possible role the individual methyl hydrogen atoms play in stabilizing the excess electron. Secondly, for the more general use of the pseudopotentials, it would be desirable for the parameters of the potential be transferable from one solvent to the other. The purpose of the present paper is to introduce such a pseudopotential, and apply it in bulk solvated electron simulations. The newly developed potential can then be used in large scale systematic simulations of negatively charged methanol clusters, the topic of our next paper.

The structure of the paper will be the following. After a brief overview of the theory and the details of the electron-methanol molecule model quantum calculations (Sec. II), we introduce and characterize the new electron-methanol molecule pseudopotential (Sec. III). In Sec. IV we illustrate the capabilities of the new potential in actual QCMD simulations of an excess electron in a methanol bath of 200 molecules. The calculations provide energetic, structural and dynamical information on the solvated electron system in methanol. The results are compared to available experimental data and earlier simulations. The main conclusions are collected in Sec. V.

II. Pseudopotential Theory and Model Calculations

In the present work we apply the electron-molecule pseudopotential theory²⁴ in the static exchange (SE) approximation.^{46,47} The development of the potential is similar to that of an electron-water molecule pseudopotential.^{31,32} We note that this approach was later generalized by Smallwood *et al.*⁴⁸ and applied for the development of an electron-tetrahydrofuran pseudopotential.⁴⁹ Nevertheless, our previous approach still remains theoretically well founded, and for the sake of consistency (and the possible transferability of the parameters) we chose to continue this in the present work.

We examine a simple computational model of a single excess electron and one neutral methanol molecule. The Schroedinger equation for the excess electron is solved in the field of the methanol molecule:

$$H|\Psi\rangle = [T + V_n + V_e + V_x + V_{conf} + V_r]|\Psi\rangle, \quad (1)$$

where T is the kinetic energy operator, and the potential contains the static nuclear attraction (V_n), the static electronic repulsion (V_e) and the non-local exchange (V_x). The operators are evaluated in the field of the frozen Hartree-Fock wave function of the neutral molecule (SE approximation). We also employ a steep, smooth confining potential, V_{conf} , in the SE Hamiltonian that keeps the electron in the vicinity of the methanol molecule,

$$V_{conf} = \frac{1}{2}k(x^8 + y^8 + z^8) \quad (2)$$

with $k = 10^{-8}$ a.u. While the confining potential basically does not perturb the potential energy surface around the methanol molecule in the chemically most relevant region, it gives rise to a steep repulsive wall at larger distances. In fact, the confining potential term can be thought of as a sensible model of the core repulsion of the surrounding methanol molecules in the bulk (see below). The last contribution of the potential energy operator of Eq. (1), a repulsive potential, V_r , is introduced in the Hamiltonian by the pseudopotential theory.^{50,51} In practice, a) the application of the Phillips-Kleinman (PK) repulsion operator⁵¹ simplifies the exact N -electron problem to a one-electron problem by creating an effective potential, and eliminating the core states of the methanol molecule, and b) mixing the core states with small linear coefficients to the first valence state removes the large oscillations of the excess electron wave function in the core region. As previously,³¹ of several physically meaningful criteria,⁵² we chose that particular linear combination of the core orbitals with the first valence orbital, which minimizes the kinetic energy of the excess state.

The technical details of solving the Schroedinger equation (Eq. (1)) are identical to that in a previous paper.³¹ The methanol wave function is taken from relatively large basis *ab initio* Hartree-Fock calculations (6-31++G(d,p) augmented by two *s*-type diffuse functions on the hydrogens with exponents 0.001 and 0.006), while the excess electron is represented by a combined basis set consisting of the methanol basis set and 7^3 evenly distributed *s*-type Gaussian functions (exponent 0.03) on a cubic grid of $20 a_0$ length placed around the methanol molecule. In the quantum calculations we used the equilibrium geometry of the OPLS (Optimized Potentials for Liquid Simulations) methanol model.⁵³ This geometry was dictated by our choice of the classical methanol potential in the subsequent QCMD simulations. Although in the computational model we considered only the *s-trans* conformation of the methyl group, we also performed test calculations on the *s-cis* conformer (see below). The resulting exact pseudo-wave function is obtained by the diagonalization of the pseudo-Hamiltonian (Eq. (1)), and a subsequent linear mixing of the core states to the first valence state to minimize the kinetic energy of the excess state. The resulting lowest energy solution of Eq. (1) provides an *exact pseudo-wave function* and the exact eigenvalue of the ground state excess electron in the SE approximation. The ground state energies for the *s-trans* methanol are $0.001117 E_h$ without the confining potential, and $0.06476 E_h$ using the confining potential. In the *s-cis* conformer, the excess electron is basically isoenergetic with $0.001079 E_h$ and $0.06451 E_h$ ground state energies, respectively. Clearly, the excess electron is bound to the molecule only by the finite basis set (in the non-confined case), or the confining potential (in the confined case) as reflected by the calculated positive eigenvalues. Figure 1 shows the excess electron density of the pseudo-wave function in various molecular directions without and with the application of the confining potential, respectively. The three directions of the illustration are along the OH bond (with the oxygen in the origin), the in-plane CH bond (with the carbon in the origin), and the dipole direction (with the center of

mass of the molecule in the origin). For comparison, we also show the electron density of the exact solution of the SE Hamiltonian without the repulsive PK potential (the LUMO of the neutral molecule). It is clear that while the large fluctuations of the exact SE wave function at the core are diminished, they do not completely disappear in the pseudo-wave function. Nevertheless, the pseudo-wave function shows proper asymptotic behavior in both cases. An additional important qualitative feature of the electron distribution is the significant electron density that appears in the direction of both the OH *and* the CH bonds.

Comparison of the confined and the non-confined cases reveals that the electron distribution of the non-confined case is very diffuse and approximately two orders of magnitude smaller than in the confined case. In addition, the use of the confining potential poses a well-defined quantum mechanical problem with solutions that are more easily interpreted than the finite-basis-bound solutions of the non-confined case. For this reason, similarly to the electron-water molecule pseudopotential,^{31,32} in the rest of the paper we consider only the confined case.

To obtain a local representation from the non-local SE Hamiltonian, the PK-repulsion and the non-local exchange operator need to be replaced to an approximate local form. For the aqueous case,³¹ we concluded that of the most commonly used approximations for the non-local repulsion and the exchange operators only the combination of the local repulsion approximation of Schnitker and Rosky²⁴ and the semiclassical exchange (SCE)⁵⁴ works satisfactorily. For the electron-methanol molecule system, this potential will be our starting point.

The Schnitker-Rosky approximation of the repulsion potential (SRR) of the pseudo-Hamiltonian is given by

$$V_r^{\text{local}}(\mathbf{r}) = -\sum_c E_c \phi_c(\mathbf{r}) \int \phi_c(\mathbf{r}') d\mathbf{r}' \quad (3)$$

where E_c 's are the eigenenergies of the methanol core states, $|\phi_c\rangle$'s. Replacement of the non-local repulsion to the SRR form reproduces the pseudo-wave function's most important features (Figure 2), and leads to $0.06460 E_h$ for the ground state energy of the excess electron in excellent agreement with the exact result.

The semiclassical exchange (SCE) operator has the following form:

$$V_x(\mathbf{r}) = -\left(\frac{2}{3}\right)\left(\frac{3\rho(\mathbf{r})}{\pi}\right)^{1/3} \quad (4)$$

where $\rho(\mathbf{r})$ is the electron density of the methanol molecule. Replacement of the non-local exchange to the local SCE exchange potential, and the application of the SRR repulsion expression in the Hamiltonian change the ground state energy to $0.06742 E_h$, few percent higher than the exact SE energy. The electron density shows pronounced changes at the core with almost complete depletion (Figure 2) indicating that the SCE potential is likely to be somewhat weaker in the plotted region of the core than the exact exchange potential. The resulting density is, however, significantly smoother than both for the exact solution and the pseudo-wave function. In addition, the SRR-SCE excess electron density reproduces the asymptotic behavior of the exact SE solution very nicely. Since the SRR-SCE local potential is theoretically well founded and reasonably reproduces the eigenenergy, and the electron density of the excess state, we decided to fit this potential in a numerical parameter optimization procedure with a function which is easily implemented in large scale molecular dynamics simulations. Before proceeding to the actual development of the potential, we make an additional remark on the applicability of other local approximations to the exchange operator. We tested three other functions for the exchange potential: the $V_x=0$ case, the Hara local exchange,⁵⁵ and the asymptotically corrected Hara exchange.⁵⁴ These functions resulted in $0.08605 E_h$, $0.08430 E_h$ and $0.05490 E_h$ ground state energies, respectively, when applied with the SR repulsion in the Hamiltonian. These values indicate either too weak or too strong

interactions. In this respect, the application of the SCE local potential represents a fair compromise among these scenarios, completely consistent with the results for the electron-water molecule model.³¹

III. A New Electron-Methanol Molecule Pseudopotential

In this section, the technical details of the formal development of the new electron-methanol molecule pseudopotential are presented. In the procedure, we approximate the SRR-SCE local potential with a simple function of the same analytical form that was used for the electron-water molecule pseudopotential.³² We note here that the procedure we follow here is also closely related to that of Schnitker and Rossky (SR) applied for the electron-water molecule pseudopotential.²⁴ Most recently, it was pointed out that there was a numerical error in the original derivation of the SR potential.^{56,57} Nevertheless, we think that this numerical error does not influence the physical contents of the arguments, and does not invalidate the basic theory itself.

Our strategy focuses on reproducing the most important features of the electron-methanol molecule SE model, the eigenenergy, and the asymptotic behavior of the wave function. After the development of the SE potential, polarization is added *a posteriori*, and is optimized to reproduce the position of the absorption spectrum of the solvated electron in methanol. It was argued previously for the electron-water pseudopotential that this procedure provides a consistent conceptual framework in association with the concept of molecular orbitals.³¹ We have to note that for the aqueous system we chose an alternative (but nearly equivalent) approach.³² For the electron-water model we were unable to fit the SRR-SCE potential *and* simultaneously provide the desired properties for the hydrated electron system (i.e. position of the absorption spectrum). Our hypothesis is that due to the few number of error functions in the linear expansion, the trial function was not flexible

enough for the aqueous system. Therefore, as a brute force approach, we simply optimized the trial function to reproduce the electron density and the ground state eigenvalue of the electron-water molecule SE model.³² Here, for the electron-methanol molecule pseudopotential we return again to the original approach that, in our view, provides a more physical insight, and attempt to fit the SRR-SCE potential.

The suitable analytical form of the pseudopotential consists of three error functions divided by the electron-site distance for each atomic site, the oxygen (r_{O}), the carbon (r_{C}), the hydroxyl hydrogen ($r_{\text{H(O)}}$) and the methyl hydrogens ($r_{\text{H(C)}}$), respectively:

$$V^i = -\frac{q_i}{r_i} \operatorname{erf}(A_{1,i} r_i) + \left[\frac{B_{1,i}}{r_i} \operatorname{erf}(B_{2,i} r_i) - \frac{B_{1,i}}{r_i} \operatorname{erf}(B_{3,i} r_i) \right] \quad (5)$$

Eq. (5) contains the partial charges of the molecular sites (q_i) taken from the OPLS potential,⁵³ and 16 adjustable parameters (4 for each type). It must be emphasized that this form of the fitting potential takes all atomic sites into account, thus providing a more detailed atomistic level description of the potential than previous potentials.³⁷ Due to the strongly repulsive potential in the core region, which practically does not influence the excess electron density outside the core, we optimized the parameters to fit the SRR-SCE potential only outside the core region (outside 1 bohr radius around the atomic centers). The optimized parameters are collected in Table I. We point out here that we did *not* optimize the parameters for the oxygen and the hydroxyl hydrogen; they were simply taken from the optimized electron-water molecule pseudopotential.³² This step clearly limits the flexibility of the fitting function (and the quality of the fit), but, at the same time, makes transferring the parameters to other systems possible. In general, we observe, that the fit of the analytical function to the SRR-SCE potential is qualitatively satisfying, providing, as expected, an average overall potential. This means that the potential removes the large oscillations and significantly decreases the repulsion at the core.⁵⁸

The main features of the fitted potential are shown in Figure 3. To test the reliability of the fitting procedure, we solved the Schrodinger equation of the excess electron on the fitted potential. The observations, that the asymptotic behavior of the wave function of the excess electron is correct, and its eigenvalue is only slightly higher ($0.06818 E_h$) than for the SRR-SCE potential, indicate that the fitted pseudopotential correctly captures the underlying basic physical aspects. A test calculation for the ground state energy of the excess electron in the *s-cis* methanol conformer essentially reproduces the isoenergetic behavior ($0.06822 E_h$) seen previously for the exact models. The fitted potential also correctly predicts the asymptotic electron density relative to the *s-cis* conformer's exact pseudo wave function and to the SRR-SCE density, as well. We can conclude that the potential model developed on the *s-trans* conformer is applicable for other rotamers of the methanol molecule.

The SE Hamiltonian of Eq. (1) does not take the induced polarization effect into account, that is, the distortion of the methanol molecule wave function by the external electric field of the excess electron. In the SE approach, polarization can only be treated separately, added to the developed SE potential *a posteriori*. For the polarization potential we apply a form similar in spirit to that proposed by Barnett *et al.* for the hydrated electron²⁶

$$V_{\text{pol}} = -\frac{\alpha_o}{2(r_o^2 + C_{1,o}^2)^2} - \frac{\alpha_c}{2(r_c^2 + C_{1,c}^2)^2} \quad (6)$$

The potential contains two terms centered on the oxygen and the carbon site. The polarizability values associated with the oxygen and the carbon ($\alpha_o=1.44 \text{ \AA}^3$, and $\alpha_c=1.7 \text{ \AA}^3$) are taken from Zhu and Cukier.³⁷ The parameters $C_{1,o}$ and $C_{1,c}$, are adjustable; they are set to reproduce the expected position of the maximum of the absorption spectrum of the solvated electron, $\sim 2.0 \text{ eV}$. We have tested eight polarization parameter sets in actual QCMD simulations.⁵⁹ The details of the simulations will be given in the next section. Of the eight

applied parameter sets, the $C_{1,O}=2.5$ and $C_{1,C}=4.4$ pair gave the best agreement with the experimental spectrum.

Figure 3 illustrates the polarization contribution and the total pseudopotential, as well. It is clear that electrostatic interactions dominate the potential. The most important feature of the potential is its deep attractive well in the OH direction (~ 60 kcal/mol), similar in magnitude to that in the electron-water potential. Another, although less strongly attractive, regions appear in the CH directions, where the depth of the well is ~ 20 kcal/mol. The attractive part associated with the methyl hydrogens may provide sufficient stabilization for the C-H bonds to effectively participate in localizing the excess electron in the bulk. Nevertheless, a qualitative comparison with a water molecule reveals that the attractive region around a methanol molecule is significantly narrower than around a water molecule. It is also evident that the interaction in the OH direction is significantly more favorable than in the dipole direction.

IV. Mixed Quantum-Classical Molecular Dynamics Simulation of a Solvated Electron in Methanol

To simulate the most important physical properties of the solvated electron in methanol, we have performed adiabatic mixed quantum-classical molecular dynamics simulations of an excess electron embedded in a classical methanol bath. The basics of the method can be found in Ref. 22. Since the details of the actual simulations are also similar to our previous hydrated electron simulations in Ref. 32, we review only the most important features of the method. The solvent bath consists of 200 methanol molecules in a cubic simulation cell. The molecular interactions are described by the all-site OPLS classical model potential with internal flexibility.⁵³ The electron is treated quantum mechanically in a plane wave basis represented on a $32 \times 32 \times 32$ grid points equidistantly distributed in the simulation

cell. The interaction between the quantum particle and the classical molecules is modeled by the present pseudopotential. We note on the calculation of the interactions that we have not corrected for the long-range interactions beyond the minimum image convention similarly to Ref. 32. The reasons why we elected to do so were the following. For the hydrated electron system we carried out simulations without³² and later with the Ewald summation,³⁵ as well. Although the ground-state energies of the excess electron differed significantly in the two simulations (-3.1 eV and -3.9 eV, respectively), the excited state energy levels were simply linearly shifted by the same constant factor. Furthermore, QCMD studies on water cluster anions indicated that the ground-state energy extrapolated to infinite cluster size predicts an even lower ground-state energy intercept, -4.4 eV.³⁵ All other properties of the hydrated electron (solvent and solute structures, solvent relaxation dynamics, and spectroscopy) were however found to be basically unaffected by the Ewald summation. We also note that the proper application of the Ewald summation for the excess electron leads to a complicated iterative procedure, which, in turn, causes numerical instabilities in the simulations. All in all, in the present work, for the solvated electron in methanol, we decided not to correct the simulations for the long-range interactions, but keep in mind that the energy levels of the excess electron (both ground-state and excited-state energy levels) will likely to be underestimated (shifted). We plan to determine the precise ground state energy in our subsequent study on methanol cluster anions.

The nuclear configurations are adiabatically propagated on the potential surfaces using the sum of classical and Hellmann-Feynman forces. The equations of motion for the nuclear evolution are integrated by the velocity Verlet algorithm⁶⁰ using a 1 fs timestep. The temperature of the methanol bath is kept constant during the simulation using the Berendsen thermostat with the coupling parameter $\tau=0.4$ ps.⁶¹ The length of the simulation box is 23.90

Å, as dictated by the OPLS simulated density of neat liquid methanol at 300 K (0.779 g/cm³).⁵³ The length of the equilibrium trajectory was 200 ps.

Figure 4 shows a representative portion of the time evolution of the ground state energy of the equilibrium excess electron at 300 K. The ground state energy is -2.1 eV, higher than that of the hydrated electron,^{32,36} but lower than computed with a previous model potential.³⁹ Of the excited states, the first and the second states are found below the vacuum level, all other higher lying states have gradually increasing positive eigenenergies. The ground state electron can be characterized by an approximately spherical electron distribution similar to found in water³² and in previous methanol simulations.³⁹ The electron distribution, characterized by its radius of gyration, is similar in size in methanol (~2.38 Å) and in water (~2.42 Å).³² More significant differences are apparent in the solvent structure around the electron. The electron-classical site pair distribution functions in methanol are shown in Figure 5. The electron-hydroxyl hydrogen function has a maximum at 2.28 Å, in excellent agreement with the experimental 2.3 Å. The position of the first maximum on the electron-oxygen function (~3.2 Å) suggests that the OH bond most likely points toward the center of the excess electron cloud. The electron-methyl hydrogen function has no sharp features, only a single broad peak between ~3.8 Å and ~5.0 Å, which is likely the average of the three rotating methyl hydrogens. Nevertheless, the beginning of this peak is only slightly farther from the electron's center than the oxygen maximum. This is a clear indication that the methyl hydrogen atoms are likely to participate to some extent in the stabilization of the excess electron, in good qualitative accord with the presence of C-H...electron interactions predicted by density functional calculations of small methanol cluster anions.²⁰ The coordination number of the first shell, obtained by the integration of the electron-molecular center-of-mass pair distribution function up to the first minimum at 4.4 Å, is ~5.1. This number once again agrees well with experiment, and is smaller than most of the simulated

values in aqueous environment (~ 6),²⁵ but greater than the coordination number computed with the predecessor of this pseudopotential developed for the electron-water molecule system (~ 4).³²

The optical absorption spectrum for the solvated electron can be seen in Figure 6. The calculation of the spectrum follows the Kubo formula in the slow-modulation limit.²³ The transition dipole moment elements were calculated in every step of the simulation from direct quadrature in the position representation. Since only the first three $s \rightarrow p$ type transitions dominate the spectral shape, in the calculation we only considered the first seven transitions. The maximum of the spectrum is found at 2.0 eV, only slightly blue-shifted relative to experiment.³ We also note that the absorption peak in methanol is ~ 0.1 eV blue-shifted compared to the hydrated electron.^{32,62} The integrated oscillator strength from the simulation (0.89) is also in reasonable agreement with the experimental value (0.69).³ These observations indicate good overall agreement with experiment. It is also noteworthy that, although the spectrum is asymmetric, the large energy tail of the spectrum is hardly developed in the simulations (~ 0.9 eV calculated vs. ~ 1.4 eV experimental half width⁴) similarly to the hydrated electron case. It has been pointed out recently⁶² that inclusion of higher transitions, and inclusion of nuclear quantum effects are necessary to significantly improve this part of the spectrum. Nevertheless, it has become apparent that, even with such improvements, the quantized spectrum is still distinctly lacking in intensity at around 2.5 eV. It is suspected that relatively asymmetric excited states may contribute to the large-energy part of the absorption band.⁶²

V. Discussion and Conclusions

We have developed a new electron-methanol molecule pseudopotential in the static exchange approximation. The route we followed is similar to that applied previously for the electron-water molecule pseudopotential.^{31,32} After the application of the Phillips-Kleinman

theorem⁵¹ and introduction of an exact pseudo-wave function, we tested several local approximations of the repulsion and the exchange operators. We have shown that of the approximate potentials, the Schnitker-Rosky local repulsion²⁴ in combination with the semiclassical exchange⁵⁴ approximates the eigenvalue and the asymptotic behavior of the wave function of the excess electron well. The final form of the new pseudopotential is based on a numerical fit of a simple function to the SRR-SCE local potential. The functional form of the pseudopotential is relatively simple and easily applicable in large scale molecular dynamics simulations. The parameters of the potential for the hydroxyl group are taken from a previous electron-water molecule pseudopotential of a similar form,³² while the parameters of the methyl group are optimized to provide the best fit to the potential. The pseudopotential is developed in combination with a classical all-site methanol potential. The pseudopotential, thus, takes all atomic sites into account and provides a more detailed atomic level picture of the interactions. Induced polarization effects are added to the potential in an *a posteriori* manner. The polarization term of the potential is chosen to optimize the position of the optical absorption band of the solvated electron in methanol in molecular dynamics simulations.

The molecular dynamics simulations performed with the final optimized parameter set provide detailed insight into the physical properties of an equilibrium excess electron in a large methanol bath. The computed structural properties are in excellent agreement with experimental observations, and are also consistent with previous hydrated electron simulations. The stabilization of the excess electron is slightly weaker in methanol than in water. The solvation structure is characterized with the dominance of OH bond orientation toward the electron, although it seems likely that C-H hydrogens also play some role in the stabilization of the excess electron. The electron itself is less diffuse than in previous models but similar in size to that in water. The average electron-oxygen distance also agrees very well with the electron spin resonance experiments of Kevan.³ As the most important difference

relative to previous models is that the ground state – excited state energy gaps are significantly increased in the present model, leading to the shift of the spectrum to its approximately proper position. This improvement was the major goal of the present work. Nevertheless, we have to make an additional remark on the issue of inhomogeneous broadening. Previous simulations suggest that the absorption spectrum of the hydrated electron is inhomogeneously broadened.⁶³ Since methanol is a slower liquid, one would expect similar behavior for the solvated electron in methanol. Polarized transient hole-burning experiments however, were not able to distinguish between the first three orthogonal transitions in water and methanol, indicating that homogeneous broadening should also play some role in the absorption spectrum.⁶⁴ Due to the complexity of the issue and the unresolved disparity with theory this problem needs further investigation, which we plan to pursue in the near future.

All these observations suggest that the present model captures the most important physical aspects of the excess electron – methanol system. In the forthcoming paper we plan to apply the pseudopotential on finite size negatively charged methanol clusters similar to previous works on hydrated electron clusters.^{33,34,35} It should be, however, emphasized that the answers we look for are necessary qualitative, in the best case, semiquantitative. The limitations of the present potential are clear from the aqueous case, starting from the static exchange approximation, the *a posteriori* introduced induced polarization effects, and the non-polarizable classical model. As a result, it has been argued previously that the similarly developed electron-water molecule pseudopotential neglects electron correlation effects, and this may cause errors for smaller system sizes.^{65,66} Another recent study pointed out the role of polarizable water models, which may also be potentially important for all cluster sizes.⁶⁷ The electron-water molecule model has nonetheless become successful. Ab initio test calculations indicated that the small cluster behavior is still reasonable, showing a reasonably

linear correlation between the ab initio stabilization energies and those calculated with the pseudopotential.³⁴ The large size behavior has been examined recently in comparison with the predictions of the dielectric continuum model of Makov and Nitzan.⁶⁸ It was found that the simulated stabilization energies of water cluster anions (both surface and interior states) approach the continuum model for large (above ~200 molecules) clusters excellently.³⁵ Furthermore, the most recent experiments on size selected water cluster anions¹⁵ seem to validate the conclusions of the simulation studies.^{33,34,35,36} Based on the similar principles of the pseudopotential development procedure, we expect a similarly reliable behavior of the present electron-molecule pseudopotential in describing finite size negatively charged methanol clusters.

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Table I. Optimized parameter set for the new electron-methanol molecule pseudopotential.

All quantities are in atomic units.

	x = O	x = H(O)	x = C	x = H(C)
q_x	-0.683	0.418	0.145	0.040
$A_{1,x}$	0.575	0.750	0.444	0.435
$B_{1,x}$	0.620	0.150	1.230	0.333
$B_{2,x}$	1.000	0.500	0.982	2.067
$B_{3,x}$	0.400	0.350	0.346	0.434
$C_{1,x}$	2.500	-	4.400	-

Figure Captions

Figure 1. Electron density of the first excess electron state in the SE approximation (dashed line) and density of the exact pseudo-wave function which minimizes the kinetic energy (solid line) without (left column) and with the application of the confining potential (right column) of Eq. (1) in various molecular directions: O-H, C-H in-plane and dipole trough the com of the molecule (from top to bottom).

Figure 2. Electron density of the exact pseudo-wave function of the excess electron which minimizes the kinetic energy (solid line), using the SR local repulsion (dashed line) and using the SR local repulsion + SCE local exchange (dotted line) in various molecular directions: O-H, C-H in-plane and dipole trough the com of the molecule (from top to bottom).

Figure 3. The fitted SE potential (dashed line), the polarization contribution (dotted line) and the total potential (solid line) in various molecular directions: O-H, C-H in-plane and dipole trough the com of the molecule (from top to bottom).

Figure 4. Time evolution of the ground state and the first excited state energies of an equilibrium solvated electron in a methanol bath.

Figure 5. Electron-molecular site pair distribution functions. Top panel: electron-hydroxyl hydrogen (bold) and electron-oxygen (dashed) distribution functions. Bottom panel: electron-methyl hydrogen (bold) and electron-center of mass of the molecule (dashed) distribution functions.

Figure 6. Optical absorption spectrum of a solvated excess electron in methanol.

Figure 1. Mones and Turi

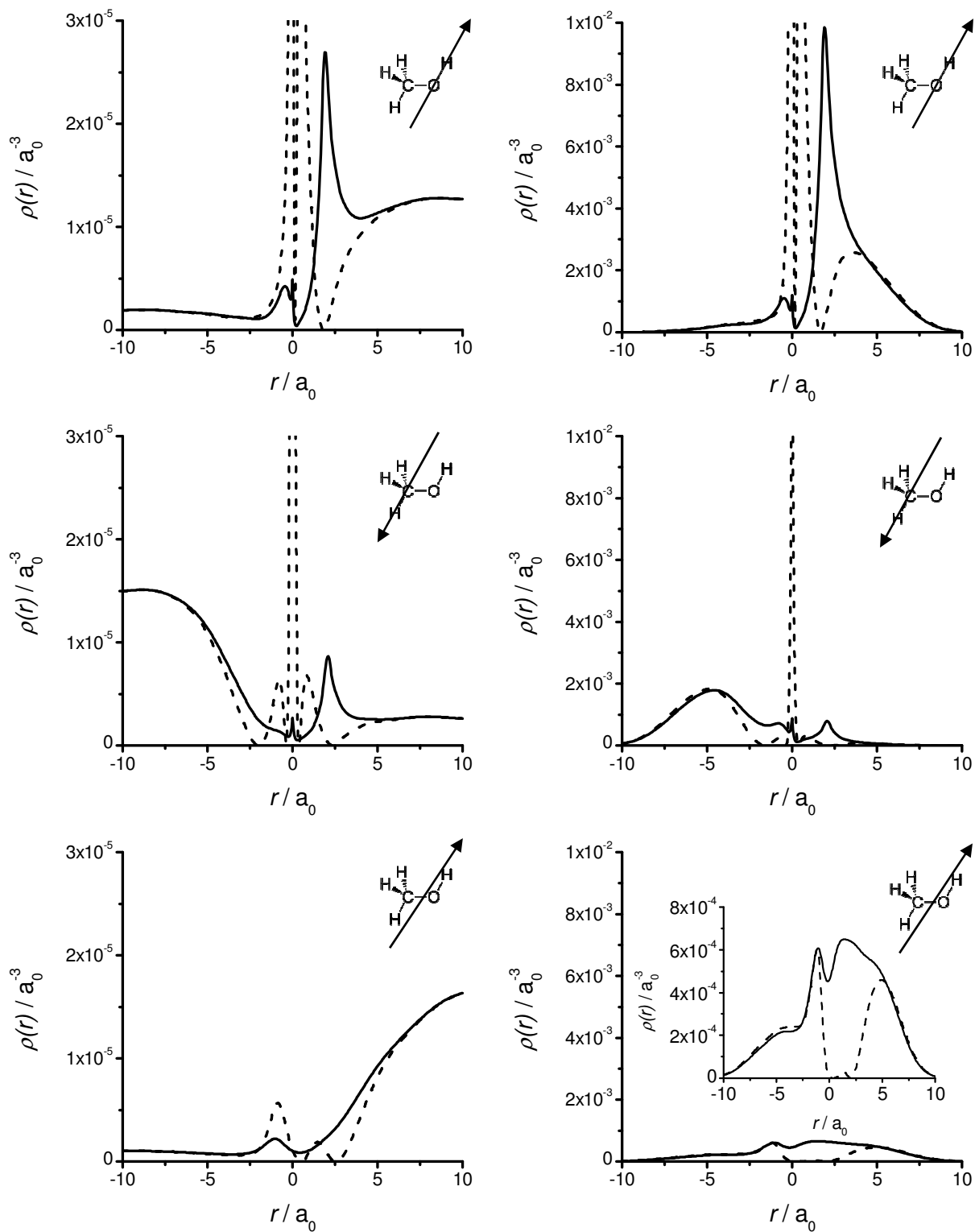


Figure 2. Mones and Turi

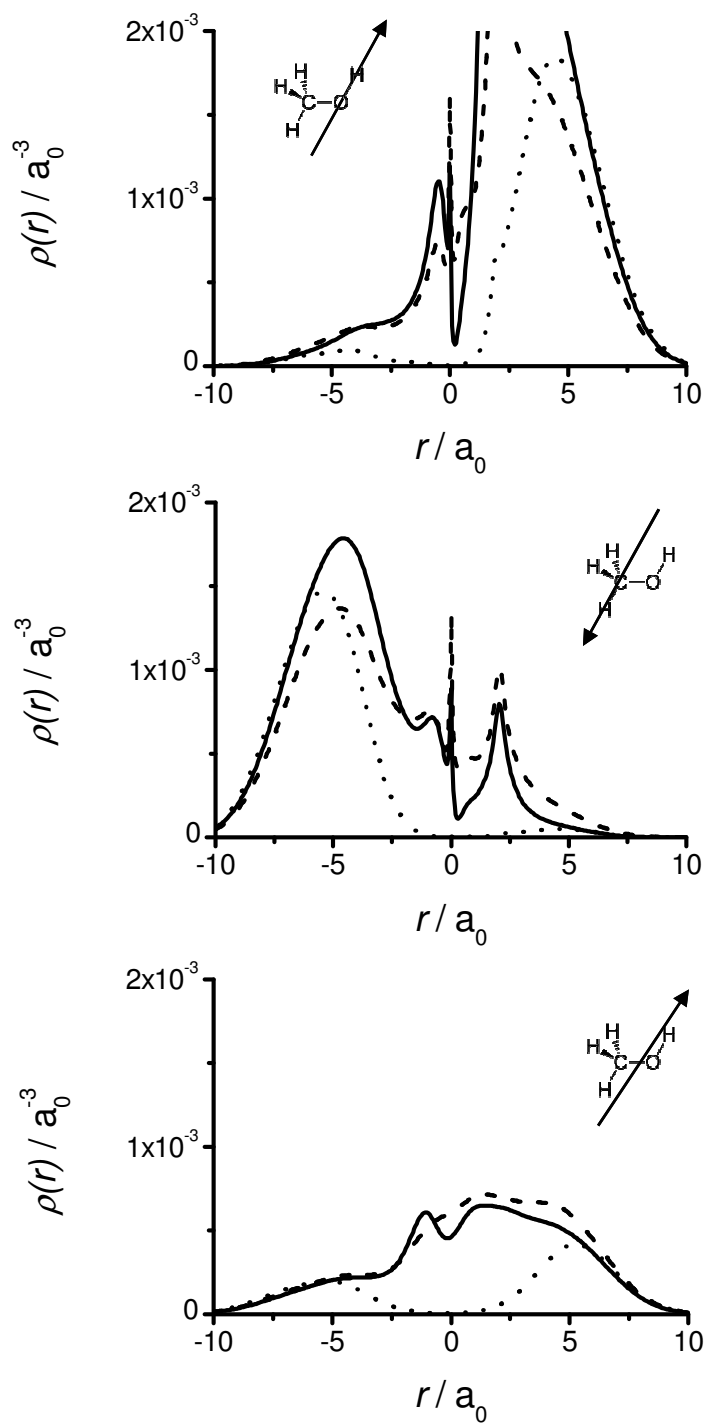


Figure 3. Mones and Turi

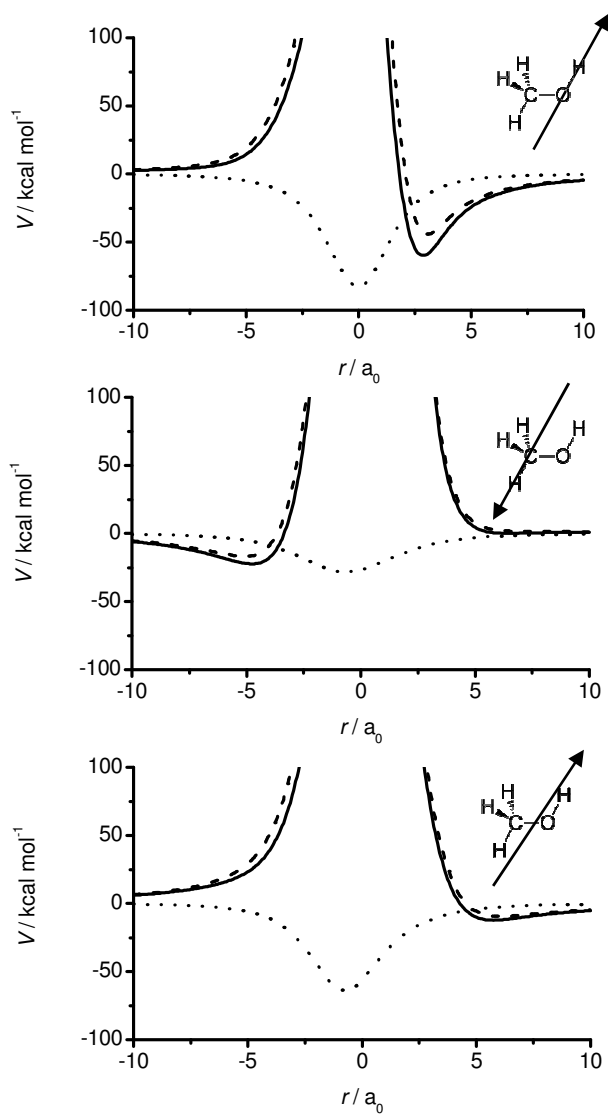


Figure 4. Mones and Turi

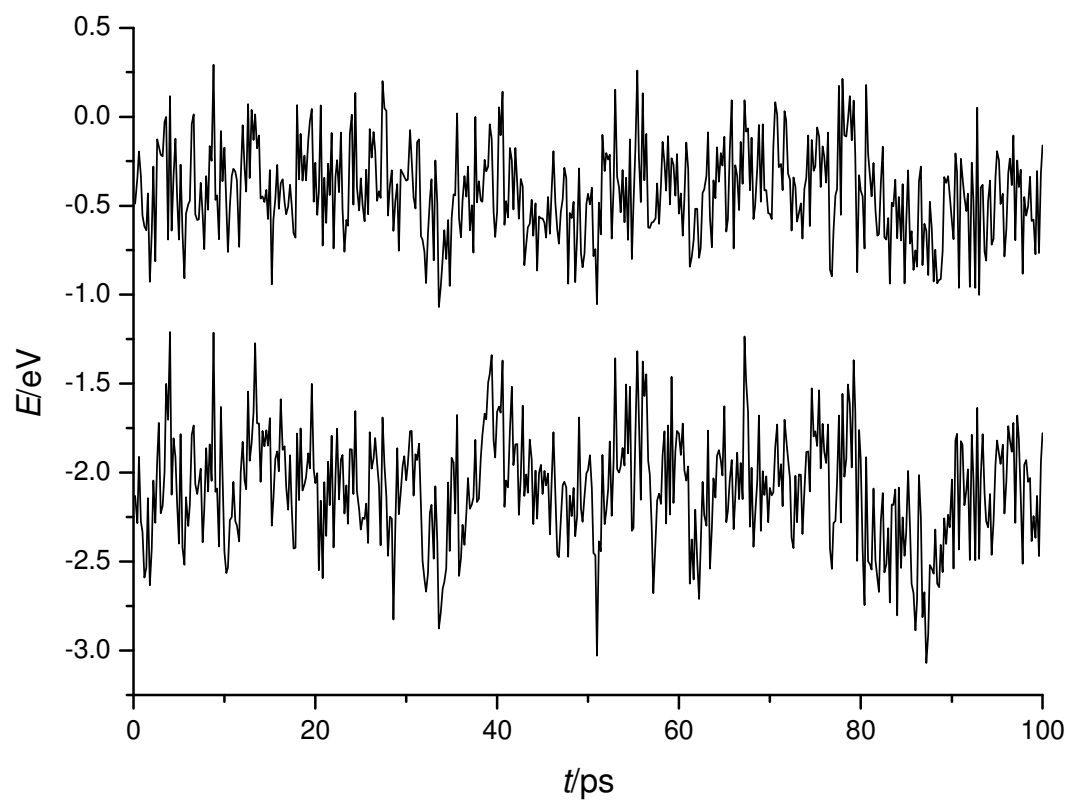


Figure 5. Mones and Turi

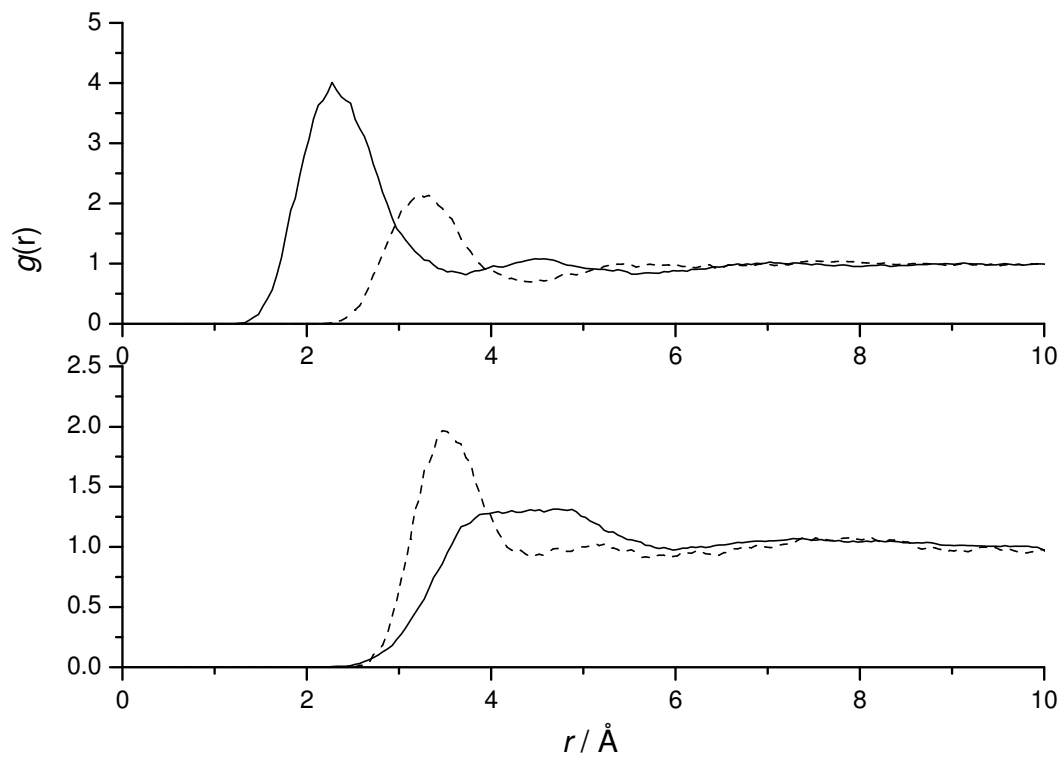
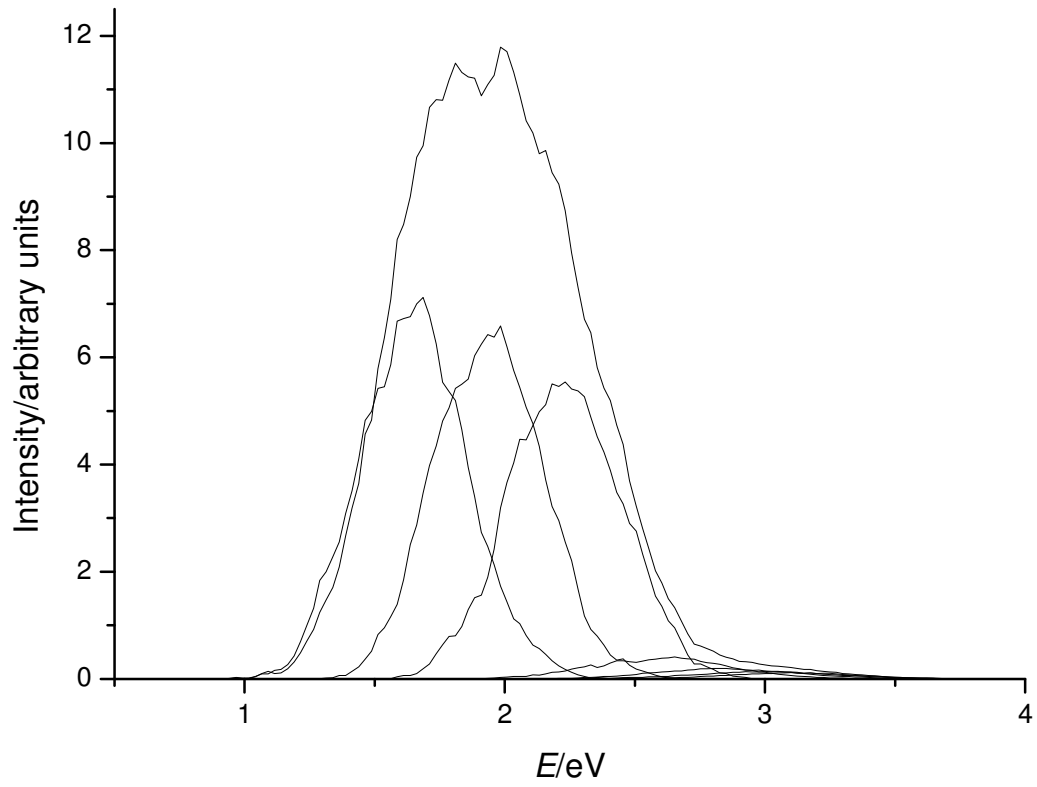


Figure 6. Mones and Turi



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