

Supporting Information

Dynamics of the Bulk Hydrated Electron from Many-Body Wave-Function Theory

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Author Contributions

V.R. Conceptualization: Lead; Formal analysis: Lead; Resources: Equal; Software: Lead; Validation: Lead; Visualization: Lead; Writing – original draft: Lead

J.V. Funding acquisition: Lead; Methodology: Supporting; Resources: Lead; Validation: Equal

J.W. Investigation: Supporting; Software: Supporting; Writing – original draft: Supporting.

SUPPORTING INFORMATION

1. MOLECULAR DYNAMICS SIMULATIONS

All canonical (NVT) simulations have been performed using the coloured noise generalized Langevin equation thermostat [1] at 300 K. The size of the periodic cell containing 47 water molecules for NVT and NVE simulations has been set to $11.295 \times 11.295 \times 11.295$

corresponding to the experimental density of the bulk liquid water at 300 K. All electronic structure calculations have been performed employing a Γ -point implementation based on the Gaussian and plane-wave (GPW) method [2] with Goedecker-Teter-Hutter type potentials [3] optimized for the corresponding functional (or Hartree-Fock) in the CP2K program [4, 5]. The Gaussian basis set was TZV2P [6] for DFT calculations, whereas the plane wave cutoff was 400 Ry. For many-body wave function calculations (MP2 and G_0W_0) correlation-consistent triple-zeta (cc-TZVP-GTH) basis sets with corresponding resolution-of-identity (RI) basis sets [15]. All basis sets have been specifically designed for the use with GTH pseudopotentials. The extra charge introduced with the access electron is treated with a compensating background.

1.1. Cavity preparation. The cavity has been prepared in several stages. First, an NPT ensemble in the periodic cell containing 48 water molecules has been equilibrated using a classical force field for 2.5 ns with a time step of 2.5 fs. Second, one of the water molecules has been substituted for the chloride anion: the resulting system has been integrated for over 8 ps with a time step of 0.5 fs at BLYP [7,8] level of electronic structure theory with the corresponding GTH pseudopotentials for the core electrons with the Grimme D3 dispersion correction (Becke-Johnson damping) [9]. Finally, the chloride was replaced by an excess electron. The system has been integrated for another 2.9 ps with a time step of 0.5 fs in an NPT ensemble (starting velocities for the remaining 47 water molecules taken from the BLYP trajectory) using the hybrid PBE0 functional with 50% of exact exchange calculated using the auxiliary density matrix method, TZV2P basis and GTH pseudopotentials. The resulting cavity is confined by four hydrogen atoms of four different water molecules, with O – H bonds pointing towards the center.

1.2. Neat liquid water structure preparation. A system containing 47 water molecules (without an excess electron) in periodic cell has been equilibrated in the NVT ensemble for 11 ps with a time step of 0.5 fs using the hybrid PBE0 functional [11,12] with 50% of exact exchange calculated using the auxiliary density matrix method [10]. Then the NVE trajectory has been integrated for another 2.5 ps employing MP2 multiple time step integrator used for the production runs as described below.

1.3. Production runs: MP2 trajectories. The MP2 MD simulations have been initialized from the preformed cavity (one trajectory of 2 ps) and from the neat bulk liquid water structure (two trajectories of 2 ps and 1 ps) and integrated in the NVE ensemble. A multiple time step scheme [13], previously proposed in the context of hybrid density functionals has been employed for integration. In this case, the fast time step (0.25 fs) corresponds to a PBEW1-D3 simulation, while the slow time step (1.5 fs) is based on MP2 as described in reference [14].

The MP2 correlation energies and forces have been computed within the RI approximation in the GWP framework [15–18]. The truncated Coulomb operator [19] has been applied for the exchange calculations with the cutoff radius approximately equal to half the length of the smallest edge of the simulation cell, 5.62 Å, together with the Schwarz integral screening with the threshold of 10^{-10} a. u. SCF convergence criterion was set to $5 \cdot 10^{-10}$ a.u. The PW cutoff for the HF part of the calculations was 500 Ry, whereas the cutoff for the correlation energy calculations was 300 Ry, respectively.

For this system size, each MP2-MD step of 1.5 fs on 256 hybrid CPU/GPU compute nodes took 12-16 minutes of wall-time.

2. GW CALCULATIONS

Band gaps have been calculated along the trajectories every 7.5 fs. For computing band gaps of the solvated electron, we employ periodic, full-frequency $G_0W_0@PBE$ calculations as implemented in CP2K [20, 21]. We employ 60 frequency points for the imaginary-frequency integration and a two-pole model for the analytic continuation of the self-energy to the real axis. The quasiparticle equation is solved self-consistently using a Newton-Raphson algorithm.

For head and wing elements of GW quantities, we employ a correction which is necessary due to the finite unit cell. This correction has been specifically derived for Gaussian basis functions [20]. For the exchange self-energy, a truncated Coulomb-potential is used with a cutoff radius of half the cell size 5.62 Å [19]. For many-body wave function calculations (MP2 and G_0W_0) correlation consistent triple-zeta (cc-TZVP-GTH) basis sets with corresponding resolution-of-identity (RI) basis sets [15]. All basis sets have been specifically designed for the use with GTH pseudopotentials. We have used correlation-consistent triple-zeta (cc-TZVP-GTH) basis sets with corresponding resolution-of-identity (RI) basis sets [15]. All basis sets have been specifically designed for the use with GTH pseudopotentials. The plane wave cutoff for the DFT part of the calculation was 500 Ry and 300 Ry for the correlated wave function part. We carefully examined the basis set convergence of the $G_0W_0@PBE$ gap and found that the $G_0W_0@PBE$ gap is already well-converged for cc-TZVP-GTH as shown in Figure S1. The difference to cc-QZVP-GTH and cc-TV5P-GRT is ca. 0.08 eV checked for a single snapshot.

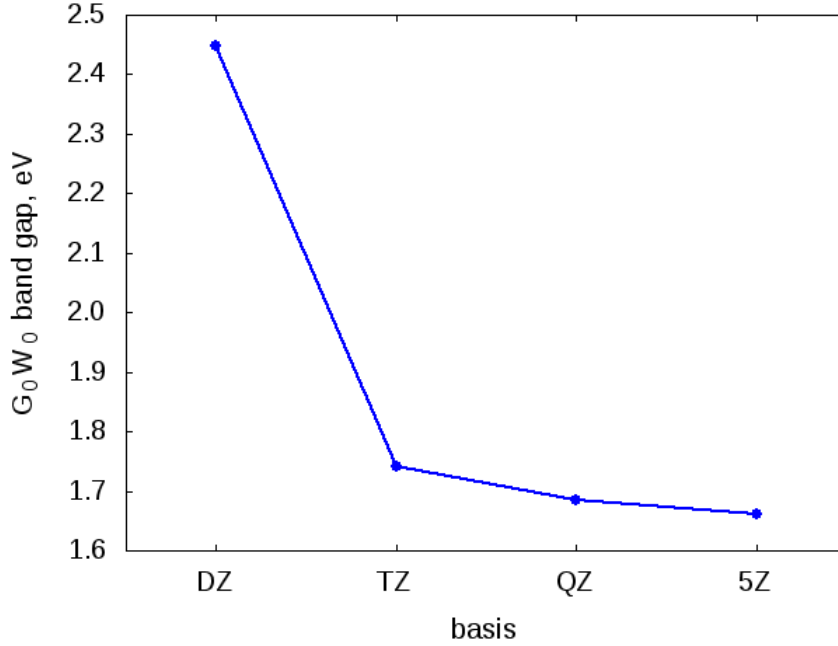


FIGURE S1. Convergence of G_0W_0 band gap with basis set size for a single snapshot.

3. VOLUMETRIC DATA ANALYSIS

3.1. Calculation of gyration radius. Since the position operator \mathbf{r} is not defined under periodic boundary conditions the gyration radius is not defined either. However, the simulation periodic cell is large enough to allow the treatment of periodic spin as non-periodic. For this purpose, the .cube files have been centered so that the spin density decays to zero on the boundaries of the cell.

The centre of spin density distribution $\rho^s(\mathbf{r})$ is given as follows:

$$(1) \quad \mathbf{r}_c = \int \rho^s(\mathbf{r})\mathbf{r}d\mathbf{r}$$

The second moment tensor reads:

$$(2) \quad \mathbf{S} = \int (\mathbf{r} - \mathbf{r}_c)(\mathbf{r} - \mathbf{r}_c)\rho^s(\mathbf{r})d\mathbf{r}$$

Then the gyration radius is calculated as:

$$(3) \quad r_g = \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2},$$

where $\lambda_1, \lambda_2, \lambda_3$ are eigenvalues of \mathbf{S} .

With the spin density on the real-space grid:

$$(4) \quad \mathbf{r}_c = \sum_{i=1}^N \rho^s(\mathbf{r}_i)\mathbf{r}_i,$$

the elements of \mathbf{S} are calculated as follows:

$$(5) \quad S_{xx} = \sum_{i=1}^N [(y_i - y_c)^2 + (z_i - z_c)^2] \rho^s(\mathbf{r}_i),$$

$$(6) \quad S_{yy} = \sum_{i=1}^N [(x_i - x_c)^2 + (z_i - z_c)^2] \rho^s(\mathbf{r}_i),$$

$$(7) \quad S_{zz} = \sum_{i=1}^N [(x_i - x_c)^2 + (y_i - y_c)^2] \rho^s(\mathbf{r}_i),$$

$$(8) \quad S_{xy} = - \sum_{i=1}^N [(x_i - x_c)^2 + (y_i - y_c)^2] \rho^s(\mathbf{r}_i),$$

$$(9) \quad S_{xz} = - \sum_{i=1}^N [(x_i - x_c)^2 + (z_i - z_c)^2] \rho^s(\mathbf{r}_i),$$

$$(10) \quad S_{yz} = - \sum_{i=1}^N [(y_i - y_c)^2 + (z_i - z_c)^2] \rho^s(\mathbf{r}_i),$$

where the summation runs over the N grid points.

3.2. Atoms in molecules analysis. The presence of the H–H chemical bonds has been revealed analyzing the topology of electron density by atoms-in-molecules (AIM) analysis [22] of periodic electron densities as performed by the CRITIC 2.0 program [23].

3.3. Visualization. Spin densities have been plotted using the VMD program [24].

4. RESULTS: PREFORMED CAVITY

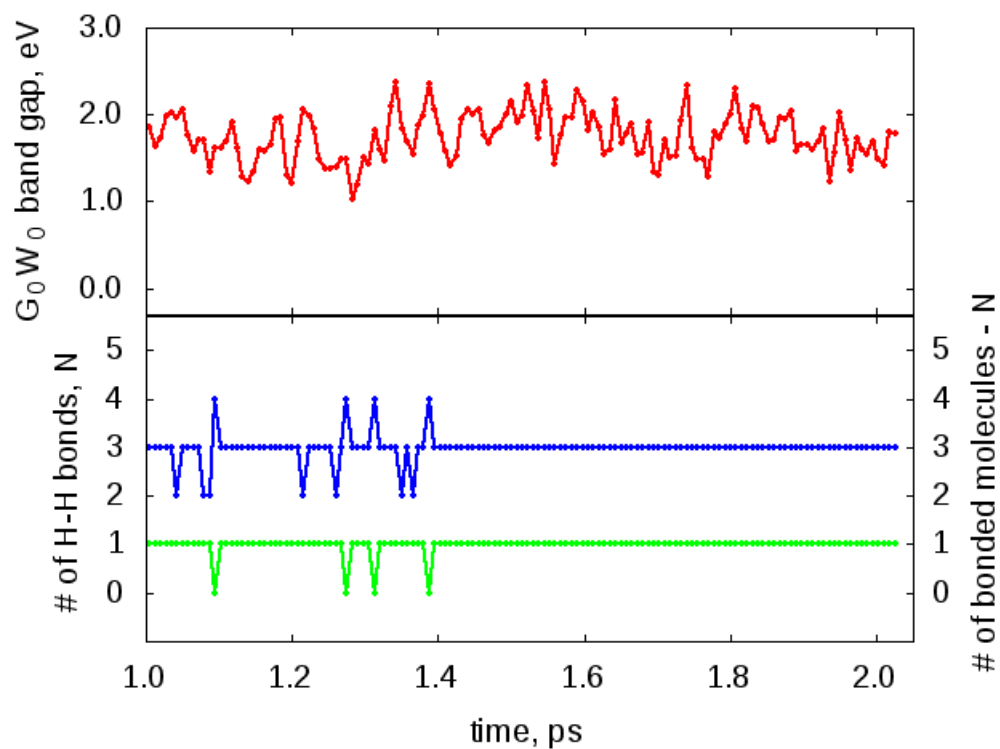


FIGURE S2. Time evolution of band gaps and bonding patterns along the second cavity formation trajectory trajectory. Data from the second half (1 ps) of the trajectory are given. Band gaps and gyration radii have been calculated along the trajectories every 7.5 fs. The bonding pattern and the gyration radius remain stable.

5. RESULTS: FIRST CAVITY FORMATION TRAJECTORY

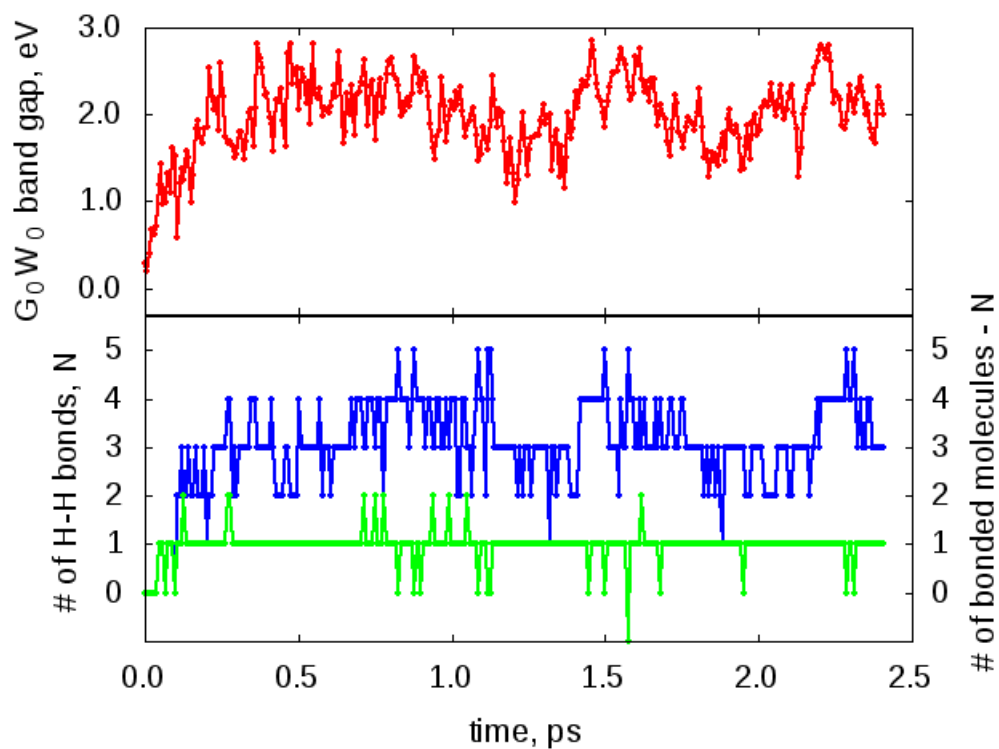


FIGURE S3. **Time evolution of band gaps and bonding patterns along the first cavity formation trajectory.** Band gaps and gyration radii have been calculated along the trajectories every 7.5 fs. Note that these results converge with time nicely to the preformed cavity results.

6. RESULTS: SECOND CAVITY FORMATION TRAJECTORY

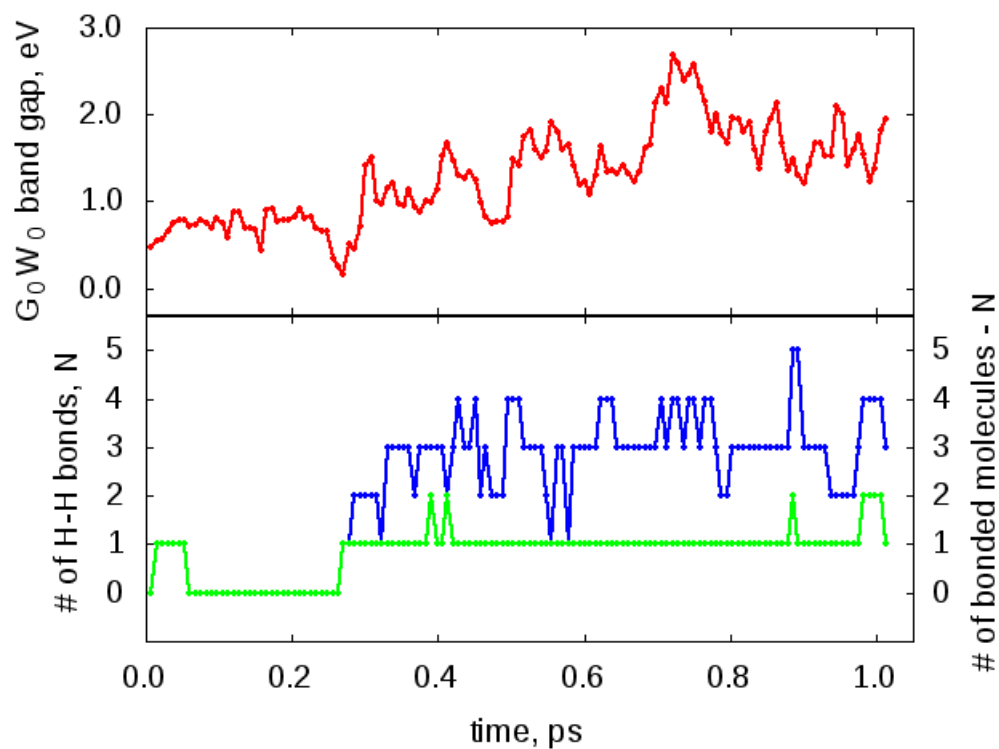


FIGURE S4. **Time evolution of band gaps and bonding patterns along the second cavity formation trajectory.** Band gaps and gyration radii have been calculated along the trajectories every 7.5 fs. Note that these results converge with time nicely to the preformed cavity results.

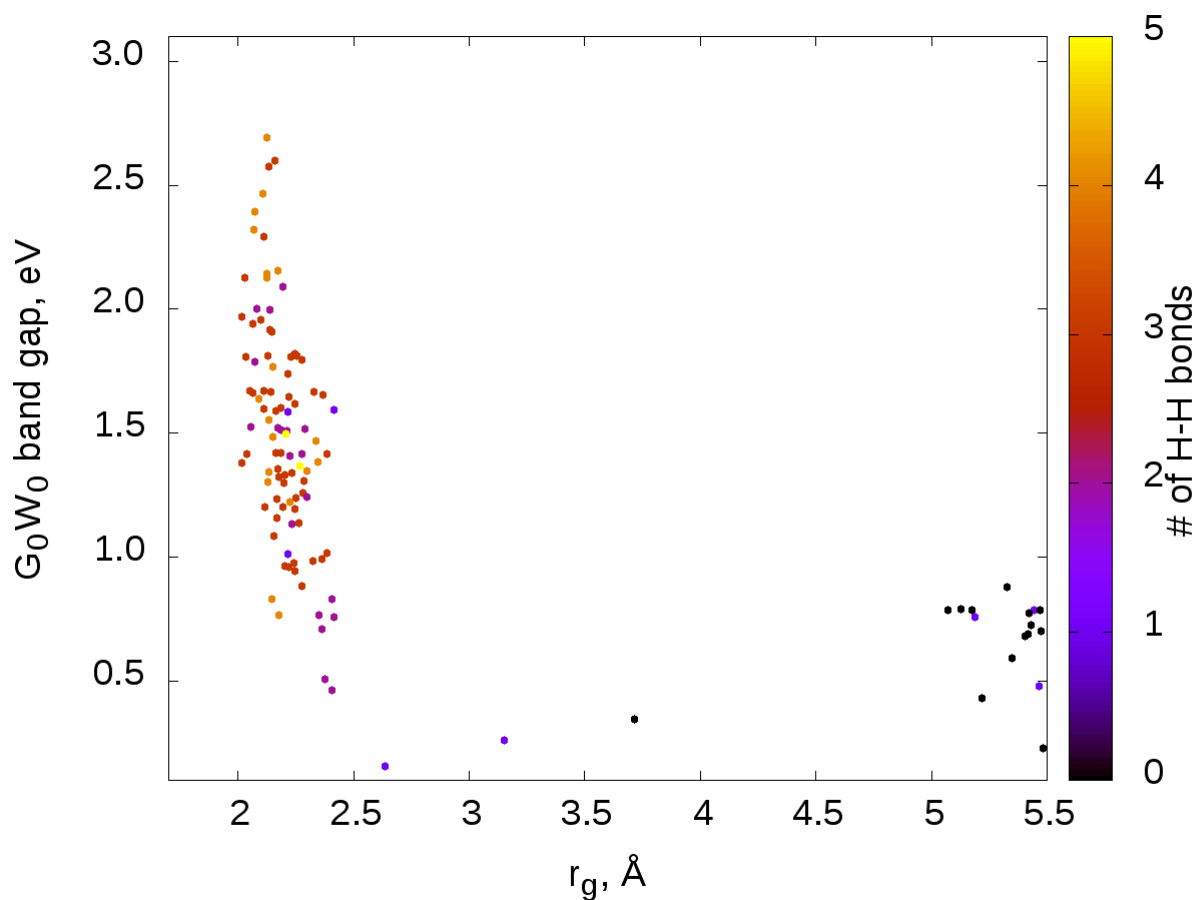


FIGURE S5. Band gaps, gyration radii, r_g of the spin density distribution and bonding of for the second cavity formation trajectory. Band gaps and gyration radii have been calculated along the trajectories every 7.5 fs. Structures with different bonding patterns have specific the spectroscopic signatures.

7. RESULTS: LOCALIZATION MECHANISM

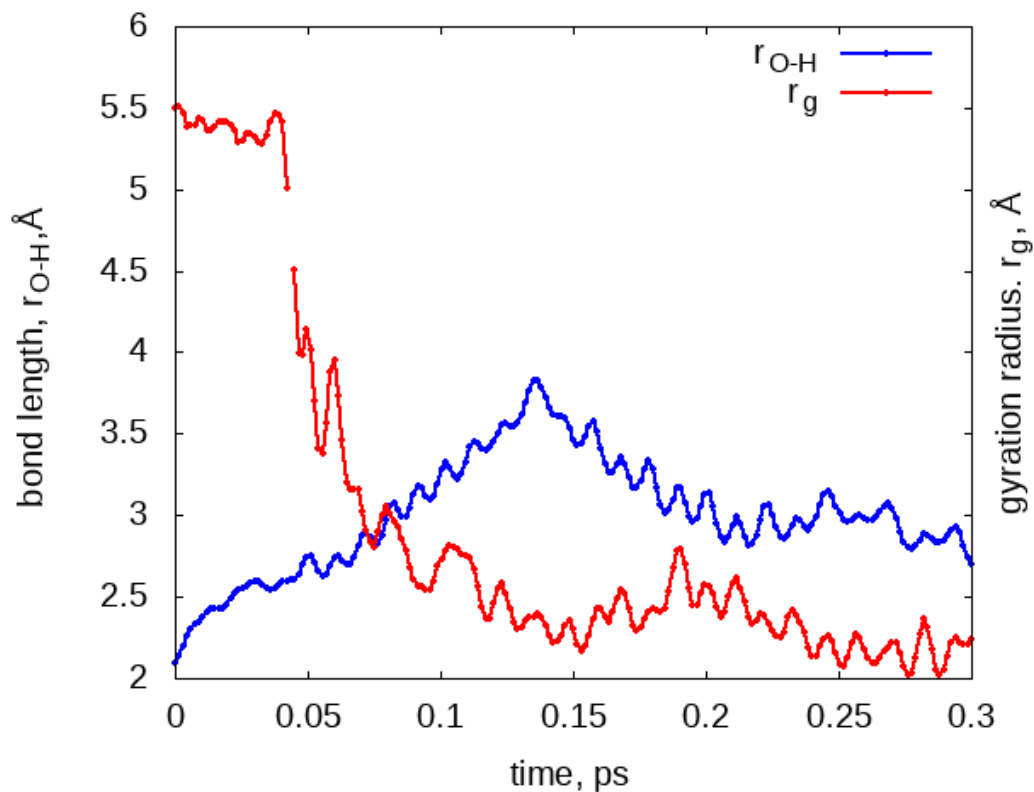


FIGURE S6. Gyration radius, r_g vs. the key O–H bond length for the first 0.3 ps of the first cavity formation trajectory, trajectory 2. One of the hydrogen bonds formed by one cavity forming water molecule with a second solvation shell molecule is elongated, creating a "trap" and launching the localization immediately as indicated by the sharp decrease of the gyration radius after the increase of the bond length.

REFERENCES

- [1] Ceriotti, M., Bussi, G. & Parrinello, M. Langevin equation with colored noise for constant-temperature molecular dynamics simulations. *Phys. Rev. Lett.* **102**, 020601 (2009).
- [2] Lippert, G., Hutter, J., & Parrinello, M. *Mol. Phys.* **92**, 477 (1997).
- [3] Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703-1710 (1996).
- [4] VandeVondele, J. et al. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Comm* **167**, 103-128 (2005).
- [5] The CP2K developers group, CP2K is freely available via the Internet at <http://www.cp2k.org/>, accessed Feb. 22, 2018.
- [6] VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **127**, 114105 (2007).
- [7] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **38**, 3098-3100 (1988).
- [8] Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789 (1988).
- [9] Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456-1465 (2011).
- [10] Guidon, M., VandeVondele, J. & Hutter, J. Auxiliary Density Matrix Methods for HartreeFock Exchange Calculations. *J. Chem. Theory Comput.* **6**, 23482364 (2010).
- [11] Perdew, J., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **78**, 3865-3868 (1996).
- [12] Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158-6170 (1999)
- [13] Guidon, M. et al. Ab initio molecular dynamics using hybrid density functionals. *J. Chem. Phys.* **128**, 214104 (2008).
- [14] Del Ben, M., Hutter, J. & VandeVondele, J. Probing the structural and dynamical properties of liquid water with models including non-local electron correlation. *J. Chem. Phys.* **143**, 054506 (2015).
- [15] Del Ben, M., Hutter, J. & VandeVondele, J. Electron correlation in the condensed phase from a resolution of identity approach based on the Gaussian and plane waves scheme. *J. Chem. Theory Comput.* **9**, 26542671 (2013).
- [16] Del Ben, M., Hutter, J. & VandeVondele, J. Forces and stress in second order Møller-Plesset perturbation theory for condensed phase systems within the resolution-of-identity Gaussian and plane waves approach. *J. Chem. Phys.* **143**, 102803-22 (2015).
- [17] Rybkin, V. V. & VandeVondele, J. Spin-unrestricted second-order Møller-Plesset (MP2) forces for the condensed phase: from molecular radicals to F-centers in solids. *J. Chem. Theory Comput.* **12**, 2214-2223 (2016).
- [18] J. Hutter et al. MP2- and RPA-Based Ab Initio Molecular Dynamics and Monte Carlo Sampling. *Handbook of Molecular Modeling*, eds. W. Andreoni, S. Yip (Springer, 2018), https://doi.org/10.1007/978-3-319-42913-7_58-1.
- [19] Guidon, M., VandeVondele, J. & Hutter, J. Robust periodic Hartree-Fock exchange for large-scale simulations using Gaussian basis sets. *J. Chem. Theory. Comput.* **5**, 30103021 (2009).
- [20] Wilhelm, J. & Hutter, J. Periodic GW calculations in the Gaussian and plane-waves scheme. *Phys. Rev. B* **95**, 235123-9.
- [21] Wilhelm, J. et al. Toward GW Calculations on Thousands of Atoms. *J. Phys. Chem. Lett.* **9**, 306-312 (2018).
- [22] Bader, R. Atoms in molecules: a Quantum theory. *Oxford University Press* (1994).
- [23] Otero-de-la-Roza, A. & Johnson, E. R. & Luana, V. Critic2: A program for real-space analysis of quantum chemical interactions in solids. *Comput. Phys. Comm.* **185**, 1007-1018 (2014).
- [24] Humphrey, W., Dalke, A. & Schulten, K.. VMD - visual molecular dynamics, *J. Molec. Graphics* **14**, 33-38 (1996). <http://www.ks.uiuc.edu/Research/vmd/>