Electron affinities of water clusters from density-functional and many-body-perturbation theory

Alex P. Gaiduk,1,* Francesco Paesani,2,† and Giulia Galli1,3,‡

1Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois 60637, United States
2University of California, San Diego, San Diego, California 92093, United States
3Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

(Dated: October 3, 2018)

In this work, we assess the accuracy of dielectric-dependent hybrid density functionals and many-body perturbation theory methods for the calculation of electron affinities of small water clusters, including hydrogen-bonded water dimer and water hexamer isomers. We show that many-body perturbation theory in the $G_0W_0$ approximation starting with the dielectric-dependent hybrid functionals predicts electron affinities of clusters within 0.1 eV of the coupled-cluster results with single, double, and perturbative triple excitations.

The calculation of electron affinities of aqueous systems is a difficult task, due to the high level of theory required to describe the electronic properties of anions and the need to achieve a tight convergence as a function of numerical parameters. Here we focus on the water dimer and hexamer and we present results for their electron affinity computed using density functional theory (DFT), many body perturbation theory ($G_0W_0$) and the CCSD(T) method. The purpose of our work is to establish the accuracy of many-body perturbation theory calculations, starting from dielectric-dependent hybrid and semi-local density functionals.

Density functional calculations were carried out using the quantum espresso code with a plane-wave cutoff of 85 Ry and Hamann–Schlüter–Chiang–Vanderbilt (HSCV) pseudopotentials; many-body perturbation theory calculations in the $G_0W_0$ approximation were performed with the west code. All calculations were performed in unit cells with size of 21.17 Å (40 a.u.); our computed energies varied by less than 0.01 eV when the cell size was increased to 31.75 Å (60 a.u.). In order to correct for spurious interactions between periodic images in plane-wave calculations, total energies and eigenvalues were computed using the Makov–Payne correction. Using Martyna–Tuckerman long-range interaction corrections instead of the Makov–Payne scheme did not change our results in any noticeable way. We checked that the electron affinities were converged with respect to the energy cutoff within 0.001 and 0.005 eV when computed as total energy differences or lowest unoccupied molecular orbital (LUMO) energy, respectively.

Quasiparticle energies were computed using the west code. We tested the convergence of $G_0W_0$ quasiparticle LUMO energies with respect to the number of eigenpotentials $N_{\text{PDEP}}$, and extrapolated our results to the infinite eigenpotential limit. Prior to this analysis, we verified that the quasiparticle energies were converged within 0.01 eV in the unit cell with the size of 21.17 Å, at the maximum number of eigenpotentials employed in this work (512). We then computed quasiparticle energies of the lowest unoccupied state using $G_0W_0$/PBE at several $N_{\text{PDEP}}$ values, and fit the results to the function $a + b/N_{\text{PDEP}}$, where $b$ represents the $G_0W_0$ energy in the limit $N_{\text{PDEP}} \to \infty$. The results denoted by “∞” in Table I indicate the extrapolated quasiparticle energies for the LUMO energy. All $G_0W_0$ calculations were performed with 256 eigenpotentials and corrected by the difference between the energies obtained at $\infty$ and $N_{\text{PDEP}} = 256 (-0.03$ eV for the dimer and $-0.15$ eV for the hexamer). All the $G_0W_0$ values reported in this work include these corrections.

The reference method chosen for benchmarking our results is the coupled cluster with singles, doubles, and perturbative correction for triples [CCSD(T)]. Coupled cluster calculations were performed using the Gaussian 09 program with tight convergence criteria for both the Hartree–Fock and CCSD iterative procedures. The accuracy of two-electron integrals was set to the $10^{-16}$ threshold (Acc2E=16 keyword) to improve convergence when using very diffuse basis sets. In all cases, we performed stability calculations on converged Hartree–Fock wavefunctions to ensure the algorithm determined a minimum of the total energy and not a saddle point.

When computing electron affinities as differences of the

| $N_{\text{PDEP}}$ | Dimer | Hexamer |
|------------------|-------|---------|
| 150              | 0.74  | 0.52    |
| 192              | 0.72  | 0.42    |
| 256              | 0.71  | 0.39    |
| 320              | 0.71  | 0.36    |
| 512              | 0.70  | 0.33    |
| \vdots           |       |         |
| $\infty$         | 0.68  | 0.24    |
TABLE II. Convergence of the calculated electron affinities of the hydrogen-bonded water dimer with respect to the basis set size used in GAUSSIAN calculations, and comparison with the plane-wave results. The ∆SCF values were computed as $E_{\text{neutral}} - E_{\text{anion}}$, where $E$ is the total energy. All values are in eV. The water dimer geometry has been taken from the S22 set and is a neutral hydrogen-bonded dimer optimized at the CCSD(T)/cc-pVQZ level of theory without counterpoise correction.

| Basis set | PBE | PBE0 | CCSD(T) |
|-----------|-----|------|---------|
| Type      | ∆SCF | $-\varepsilon_{\text{LUMO}}$ | ∆SCF | $-\varepsilon_{\text{LUMO}}$ | ∆SCF |
| aug-cc-pVVDZ | -0.22 | 1.27 | -0.33 | 0.62 | -0.499 |
| d-aug-cc-pVDZ | 0.12 | 1.28 | 0.06 | 0.66 | -0.070 |
| t-aug-cc-pVDZ | 0.24 | 1.28 | 0.13 | 0.66 | -0.005 |
| q-aug-cc-pVDZ | 0.31 | 1.28 | 0.18 | 0.66 | 0.0040 |
| 5-aug-cc-pVDZ | 0.33 | 1.28 | 0.20 | 0.66 | 0.0048 |
| 6-aug-cc-pVDZ | 0.34 | 1.28 | 0.21 | 0.66 | 0.0051 |
| aug-cc-pVTZ | -0.14 | 1.26 | -0.24 | 0.62 | -0.385 |
| d-aug-cc-pVTZ | 0.13 | 1.26 | 0.07 | 0.64 | 0.0055 |
| t-aug-cc-pVTZ | 0.23 | 1.26 | 0.13 | 0.64 | 0.0030 |
| q-aug-cc-pVTZ | 0.30 | 1.26 | 0.18 | 0.64 | 0.0046 |

* Results are converged with respect to the kinetic energy cutoff to within 0.001 eV for ∆SCF energy differences and 0.005 eV for LUMO energies.

Table III. Accuracy of various DFT approximations and G0W0 calculations starting from PBE and hybrid functionals, compared to CCSD(T), for the calculations of the electron affinity of water dimer. Similar to Table II, ∆SCF values for the electron affinity are defined as $E_{\text{neutral}} - E_{\text{anion}}$, where $E$ denotes the total energy. The G0W0 results were corrected by 0.03 eV (negative of the −0.03 eV correction for the quasiparticle energy of the dimer) to extrapolate to the infinite number of eigenpotentials, as determined in Table I. All values are in eV.

| Approximation | ∆SCF | $-\varepsilon_{\text{DFT}}^{\text{LUMO}}$ | $-\varepsilon_{\text{G0W0}}^{\text{LUMO}}$ |
|---------------|------|-------------------------------|-------------------------------|
| PBE           | 0.32 | 1.25                          | -0.62                         |
| PBE0          | 0.19 | 0.65                          | -0.45                         |
| RSH (0.565)$^a$ | 0.26 | 0.18                          | -0.08                         |
| RSH (1.0)$^b$ | 0.38 | 0.03                          | 0.05                          |

| CCSD(T)       | 0.0051$^c$ |

$^a$ Range-separated functional defined with the fraction of the Hartree–Fock exchange chosen to be the same as for bulk liquid water (0.565)$^{12}$ and screening parameter of 0.58.
$^b$ Range-separated functional defined for finite systems (fraction of exact exchange equal to 1) and screening parameter of 0.58.$^c$

$^c$ Value from Table II computed using 6-aug-cc-pVVDZ basis set.

Plane-wave basis set with the cutoff of 85 Ry provides an almost complete basis-set limit for the electron affinities, as shown by the comparison of the results obtained using the largest GTO and PW basis sets. This implies that (i) the protocol for computing the total energies for water clusters in plane waves, including the finite-size correction of Makov–Payne, is reliable for the systems studied here; and (ii) the basis sets chosen here will provide accurate representation of the anions for benchmarking our DFT and GW methods against the coupled-
TABLE IV. Convergence of CCSD(T) electron affinities for a series of hexamers with respect to the basis set size. All values were computed as differences of the total energies $E_{\text{neutral}} - E_{\text{anion}}$ and are reported in eV. The geometries of the water hexamers are shown in Figure 1 and listed in Appendix A.

| Basis set     | Book   | Cage   | Prism  | Ring   |
|---------------|--------|--------|--------|--------|
| aug-cc-pVDZ   | −0.087 | −0.175 | −0.117 | 0.070  |
| t-aug-cc-pVDZ | 0.087  | 0.049  | 0.077  | 0.152  |
| q-aug-cc-pVDZ | 0.088  | 0.050  | 0.077  | 0.172  |

cluster method.

We first checked the convergence of the CCSD(T) calculations with respect to the basis set size for the water dimer. Our results, reported in the last column of Table II, confirmed that quadruply-augmented basis sets provide essentially converged CCSD(T) electron affinity. Even for triply-augmented basis sets, the error in $\Delta$SCF values is just 0.01 eV. We compared our results to those of Kim et al.,\textsuperscript{14} who used TZ(2df,2pd)+(3s3p,3s) basis set at the CCSD(T) level of theory and obtained $\Delta A = 0.0044$ eV. The TZ(2df,2pd)+(3s3p,3s) basis is essentially the same as the cc-pVTZ basis augmented with 3 sets of diffuse s and p functions for oxygen, and 3 sets of diffuse s functions for hydrogen. Their basis set should be comparable to, but slightly smaller than the q-aug-cc-pVTZ basis set used here, explaining the similarity of the value 0.0044 eV obtained in Ref. 14 and our value of 0.0046 eV obtained using the q-aug-cc-pVTZ basis set. Overall, we consider the value of 0.0051 eV as an accurate CCSD(T) reference value for the electron affinity of the dimer, which will be used for comparison with our DFT and MBPT results.

Table III reports the electron affinities computed using PBE,\textsuperscript{15,16} PBE0,\textsuperscript{17} and RSH\textsuperscript{11} functionals as the difference of total energies ($\Delta$SCF), and as a DFT or $G_0W_0$ LUMO energy. We used the RSH functional with two different values of the dielectric screening: the same as used for bulk water,\textsuperscript{12} and the one used for molecules (i.e. that of vacuum) in the original definition of RSH reported in Ref. 11. Figure 2 summarizes deviations of all these quantities from the CCSD(T) value. As expected, the largest errors are found for the DFT LUMO values, due to the fact that generalized-gradient approximations such as PBE lack piecewise linearity of the total energy with respect to the number of electrons $N$, leading to an inaccurate approximation of the vertical electron affinity by the LUMO energy.\textsuperscript{18} $\Delta$SCF calculations yield improved results, as total energies are piecewise linear with respect to $N$ by construction, and their accuracy is limited only by the accuracy of a given functional. Electron affinities from $G_0W_0$ calculations are less accurate than $\Delta$SCF results for PBE and PBE0 approximations but are equally or more accurate than DFT results for RSH functionals with different fractions of the exact exchange. This is likely because the dielectric-constant-dependent functionals have lower self-interaction error than the PBE and PBE0 functionals, and thus provide a more realistic starting point for $G_0W_0$ corrections. We note that DFT approximations consistently overestimate the electron affinity of the dimer compared to the CCSD(T) value, while $G_0W_0$ yields the wrong sign for RSH (0.565) and a slight overestimate for RSH (1.0). Overall, deviation of the $G_0W_0$/RSH values from the CCSD(T) reference for the water dimer is less than 0.1 eV, irrespective of the sign.

In addition to the dimer, we computed the electron affinities of larger water hexamers shown in Figure 1. Following the convergence study reported in Table II, we computed CCSD(T) electron affinities using the q-aug-cc-pVDZ basis set, which turned out to be converged within 0.02 eV with respect to the number of diffuse functions (see Table IV). The results of our analysis for water hexamers are reported in Table V and Figure 3, showing trends similar to the dimer for the relative accuracy of various approximations. We found again that $G_0W_0$/RSH protocol is the most accurate, with an average deviation of the electron affinities from the CCSD(T) results of only 0.01 eV for RSH (0.565) and of 0.11 eV for RSH (1.0). Overall, we showed that many-body perturbation theory calculations coupled with dielectric-constant-dependent functional RSH predicts the electron affinities of water clusters within 0.1 eV from the golden standard of quantum chemistry, CCSD(T).

ACKNOWLEDGMENTS

The authors gratefully acknowledge helpful discussions with Marco Govoni and Nicholas Brawand. APG and GG were supported by MICCoM as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division (5J-30161-0010A). APG was also supported by the postdoctoral fellowship from the Natural Sciences
TABLE V. Electron affinities computed for water hexamers using various DFT approximations and G₀W₀ calculations, compared to CCSD(T) results. The coupled cluster electron affinities are the values reported in Table IV and computed using the q-aug-cc-pVDZ basis set. As in Table II, the ΔSCF values were computed as $E_{\text{neutral}} - E_{\text{anion}}$, where $E$ is the total energy.

| Hexamer | Functional | ΔSCF | $\varepsilon_{\text{LUMO}}$ | $\varepsilon_{\text{LUMO}}$ | CCSD(T) |
|---------|------------|------|----------------------------|----------------------------|----------|
| Book    | PBE        | 0.32 | 1.48                      | -0.24                      | 0.088    |
|         | PBE0       | 0.23 | 0.86                      | -0.14                      |          |
|         | RSH (0.565)| 0.18 | 0.32                      | 0.09                       |          |
|         | RSH (1.0)  | 0.37 | 0.05                      | 0.20                       |          |
| Cage    | PBE        | 0.29 | 1.38                      | -0.33                      | 0.050    |
|         | PBE0       | 0.21 | 0.77                      | -0.21                      |          |
|         | RSH (0.565)| 0.20 | 0.25                      | 0.08                       |          |
|         | RSH (1.0)  | 0.38 | 0.05                      | 0.19                       |          |
| Prism   | PBE        | 0.32 | 1.45                      | -0.27                      | 0.077    |
|         | PBE0       | 0.22 | 0.83                      | -0.16                      |          |
|         | RSH (0.565)| 0.17 | 0.30                      | 0.09                       |          |
|         | RSH (1.0)  | 0.38 | 0.05                      | 0.20                       |          |
| Ring    | PBE        | 0.50 | 1.85                      | 0.01                       | 0.172    |
|         | PBE0       | 0.36 | 1.19                      | 0.03                       |          |
|         | RSH (0.565)| 0.23 | 0.52                      | 0.16                       |          |
|         | RSH (1.0)  | 0.14 | 0.08                      | 0.24                       |          |

and Engineering Research Council of Canada. FP was supported by the National Science Foundation through grant CHE-1453204 and used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation through grant ACI-1053575. An award of computer time was provided by the INCITE program. This research used resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under contract DEAC02-06CH11357.

Appendix A  WATER HEXAMERS

All molecular geometries are in in xyz format, with the coordinates given in Angstroms.

| Hexamer | O     | H     |
|---------|-------|-------|
| Book    | 0     | 0.274 | 1.424 | 1.149 |
|         | H     | 0.301 | 2.281 | 1.584 |
|         | H     | 1.065 | 1.395 | 0.561 |
|         | O     | -0.182| -1.395| 1.046 |
|         | H     | -1.007| -1.426| 0.528 |
|         | H     | -0.094| -0.465| 1.303 |
|         | O     | -1.922| 1.452 | -0.590|
|         | H     | -1.725| 2.060 | -1.310|
|         | H     | -1.152| 1.512 | 0.006 |
|         | O     | -2.533| -1.178| -0.486|
|         | H     | -3.310| -1.150| 0.071 |
|         | H     | -2.345| -0.235| -0.685|
|         | O     | 2.359 | 1.101 | -0.549|
|         | H     | 2.137 | 1.586 | -1.351|
|         | H     | 2.265 | 0.152 | -0.753|
|         | O     | 2.003 | -1.665| -0.565|
|         | H     | 2.686 | -1.978| 0.028 |
| Cage    | O     | 0.668 | -1.715| -0.324|
|         | H     | 0.888 | -2.653| -0.324|
|         | H     | 1.530 | -1.248| -0.246|
|         | O     | -0.600| 0.461 | -1.631|
|         | H     | -1.491| 0.364 | -1.254|
|         | H     | -0.184| -0.399| -1.455|
|         | O     | 0.704 | 1.769 | 0.353 |
|         | H     | 0.776 | 2.712 | 0.212 |
|         | H     | 0.238 | 1.400 | -0.435|
|         | O     | -0.833| -0.335| 1.654 |
|         | H     | -0.335| 0.487 | 1.561 |
|         | H     | -0.312| -0.969| 1.129 |
|         | O     | 2.829 | -0.072| -0.059|
|         | H     | 3.390 | -0.383| 0.659 |
|         | H     | 2.313 | 0.674 | 0.286 |
|         | O     | -2.928| 0.016 | -0.061|
|         | H     | -3.279| -0.858| -0.230|
|         | H     | -2.258| -0.115| 0.647 |
| Prism   | O     | -1.409| -0.377| 1.473 |
|         | H     | -2.071| -0.903| 1.937 |
|         | H     | -0.529| -0.766| 1.643 |
|         | O     | -1.599| -0.612| -1.295|
|         | H     | -2.396| -1.046| -1.619|
|         | H     | -1.654| -0.691| -0.322|
|         | O     | -0.931| 1.906 | -0.094|
|         | H     | -1.269| 1.374 | -0.827|
|         | H     | -1.226| 1.389 | 0.673 |
|         | O     | 1.263 | -1.095| 1.417 |
|         | H     | 1.596 | -0.202| 1.266 |
|         | H     | 1.243 | -1.449| 0.511 |
Appendix B  6-AUG-CC-PVDZ BASIS SET
Appendix C  Q-AUG-CC-PVTZ BASIS SET

-H  0
S  3  1.00  33.87000000 0.0060680  5.09500000 0.0453080  1.15900000 0.2028220  
S  1  1.00  0.32580000 1.0000000  
S  1  1.00  0.10270000 1.0000000  
S  1  1.00  0.02526000 1.0000000  
S  1  1.00  0.00612000 1.0000000  
S  1  1.00  0.00152670 1.0000000  
S  1  1.00  0.00037530 1.0000000  
P  1  1.00  1.40700000 1.0000000  
P  1  1.00  0.38800000 1.0000000  
P  1  1.00  0.10200000 1.0000000  
P  1  1.00  0.02680000 1.0000000  
P  1  1.00  0.00704160 1.0000000  
P  1  1.00  0.00185000 1.0000000  
D  1  1.00  1.05700000 1.0000000  
D  1  1.00  0.24700000 1.0000000  
D  1  1.00  0.05770000 1.0000000  
D  1  1.00  0.01347890 1.0000000  
D  1  1.00  0.00314870 1.0000000  
S  8  1.00  15330.00000000 0.0000000  
S  8  1.00  2299.00000000 0.0000000  
S  8  1.00  522.40000000 0.0000000  
S  8  1.00  147.30000000 0.0000000  
S  8  1.00  47.55000000 0.0000000  
S  8  1.00  16.76000000 0.0000000  
S  8  1.00  6.20700000 0.0000000  
S  8  1.00  0.68820000 0.0000000  
-0  0
S  8  1.00  15330.00000000 0.0000000  
S  8  1.00  2299.00000000 0.0000000  
S  8  1.00  522.40000000 0.0000000  
S  8  1.00  147.30000000 0.0000000  
S  8  1.00  47.55000000 0.0000000  
S  8  1.00  16.76000000 0.0000000  
S  8  1.00  6.20700000 0.0000000  
S  8  1.00  0.68820000 0.0000000  
****
E-mail: agaiduk@uchicago.edu
† E-mail: fpaesani@ucsd.edu
‡ E-mail: gagalli@uchicago.edu

1 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter 21, 395502 (2009).
2 D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).
3 D. Vanderbilt, Phys. Rev. B 32, 8412 (1985).
4 west code (version 1.0.1): http://west-code.org/ (retrieved October 3, 2018).
5 G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995).
6 G. J. Martyna and M. E. Tuckerman, J. Chem. Phys. 110, 2810 (1999).
7 M. Govoni and Giulia Galli, unpublished.
8 P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Phys. Chem. Chem. Phys. 8, 1985 (2006).
9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klein, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, “Gaussian 09, Revision D.01,” Gaussian Inc., Wallingford, CT (2013).
10 D. E. Woon and T. H. Dunning, J. Chem. Phys. 100, 2975 (1994).
11 J. H. Skone, M. Govoni, and G. Galli, Phys. Rev. B 93, 235106 (2016).
12 A. P. Gaiduk, T. A. Pham, M. Govoni, F. Paesani, and G. Galli, Nat. Commun., accepted (2017).
13 J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys. 10, 6615 (2008).
14 J. Kim, J. Y. Lee, K. S. Oh, J. M. Park, S. Lee, and K. S. Kim, Phys. Rev. A 59, R930 (1999).
15 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
16 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
17 C. Adamo and V. Barone, J. Chem. Phys. 110, 6158 (1999).
18 J. P. Perdew, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982).
FIG. 2. Deviations of the electron affinities (EA) computed as $\Delta$SCF values ($E_{\text{neutral}} - E_{\text{anion}}$), and negatives of the DFT LUMO energies and $G_0W_0$ quasiparticle energies, from the CCSD(T) value for the water dimer. The bars represent differences between the DFT or $G_0W_0$ values reported in Table III from the reference CCSD(T) EA energy of 0.0051 eV. The PBE, PBE0, and RSH functionals are defined in Refs. 15, 17, and 11, respectively. The number within brackets for the RSH functional is the value of the dielectric screening (see text).

FIG. 3. Average deviations of electron affinities computed as $\Delta$SCF values ($E_{\text{neutral}} - E_{\text{anion}}$), and negatives of the DFT LUMO energies and $G_0W_0$ LUMO energies from CCSD(T) values for the four water hexamers reported in Table V. The bars represent average differences between the DFT or $G_0W_0$ results from the reference CCSD(T) EA energies reported in Table V. The PBE, PBE0, and RSH functionals are defined in Refs. 15, 17, and 11, respectively. The number within brackets for the RSH functional is the value of the dielectric screening (see text).