Supplementary infomation for 'Real single ion solvation free energies with quantum mechanical simulation'

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Surface potential definitions

Tables 1 and 2 summarize the definitions of the surface potentials used throughout this paper. See Ref. 1 for a full discussion of how to calculate these terms.

Table 1: Surface potential definitions

Type	Expression
Dipolar	$\phi_{\mathrm{D}} = -\epsilon_0^{-1} \int_0^{z/2} dz P_z(z)$
Bethe	$\phi_{\mathrm{B}} = -\frac{1}{6V\epsilon_0} \sum_i q \langle r^2 \rangle_i$
Cavity	$\phi_{\mathrm{C}} =$ See SI of Ref. 2
Net	$\Phi^{\mathrm{HW}} = \phi_{\mathrm{C}} + \phi_{\mathrm{D}}$
Total	$\Delta\phi = \phi_{\mathrm{D}} + \phi_{\mathrm{B}} = -\epsilon_0^{-1} \int_{z_l}^{z_v} dz \rho(z) z$

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Table 2: Four types of solvation free energies

Type	Expression
Real	μ_X^*
Intrinsic	$\mu_X^{*\mathrm{Int}} = \mu_X^* - q_I \phi_\mathrm{D}$
Bulk	$\mu_X^{*\mathrm{Bulk}} = \mu_X^* - q_I \Phi^\mathrm{HW}$
Ewald	$\mu_X^{*\mathrm{Ewald}} = \mu_X^* - q_I \phi_\mathrm{D} - q_I \phi_\mathrm{B} + \mu_{\mathrm{Ew\text{-}Corr}}$

Calculation details

The free energy of placing a hydrogen nucleus with its charge scaled to zero is non-negligible when calculated with CP2K. This is a numerical issue associated with the pseudo-potential of the core of the hydrogen atom and the dispersion interaction calculation. This term can be easily estimated using the following relationship:

$$\mu_{\mathrm{PC}(0)}^* = -k_\mathrm{B} T \ln \left\langle \exp^{-\beta U_{\mathrm{PC}}(0)} \right\rangle_{U_{\mathrm{Cav}}} \tag{1}$$

or its inverse:

$$\mu_{\mathrm{PC}(0)}^* = k_\mathrm{B} T \ln \left\langle \exp^{\beta U_{\mathrm{PC}}(0)} \right\rangle_{U_{\mathrm{Cav}} + U_{\mathrm{PC}}(0)} \tag{2}$$

where $U_{\mathrm{PC}}(0)$ is the energy change on placing the neutral hydrogen nucleus in the cavity. This term is entirely unphysical and so we do not want to include it in the charging free energy. It will not contribute to the final energy as its contribution will be cancelled out when the hydrogen atom is swapped out for the real ion in the following step. This contribution is therefore combined with the quantum mechanical free energy term in the results given below.

The Bethe potential was calculated for several situations to examine how much it varies. The results are presented in Table 3. It is clear that there is a small difference when the real ion is present compared to when the charged hard sphere is present. This leads to a small correction of 0.8 kJ mol^{-1} and -5.4 kJ mol^{-1} to the values reported in Ref. 1 for the 2 Å and 2.6 Å charged hard sphere solvation free energies. See Ref. 1 for details regarding the computation of the Bethe potential.

Table 3: Bethe potentials (ϕ_B).

Solute	$\phi_B(V)$
R_{HS} = 2.0 Å, q = 0	3.407
R_{HS} = 2.0 Å, q = 1	3.409
R_{HS} = 2.6 Å, q = 0	3.414
R_{HS} = 2.6 Å, q = −1	3.402
Li$^+$	3.417
F$^-$	3.458

To calculate the cavity formation energy we had to determine the position of the hard sphere repulsion. The hard sphere repulsion does not occur at precisely R_{Cav} as this potential is not infinitely sharp. We therefore specify a range over which the solute-oxygen radial distribution function is increasing sharply and use the middle of this range in the cavity formation energy expression calculated in Ref. 3. The energy at either extreme of this range provides an uncertainty in this value. For lithium the range is 2.07 to 2.12 for fluoride the range is 2.69 to 2.71. The same cavity radius range is used to determine the energy of relaxing the hard sphere constraint and the uncertainty in this energy.

Full Contributions

Table 4 and Table 5 give a much more detailed breakdown of the contributions to the solvation free energies for both lithium and fluoride respectively. Adding all of the values in the final column gives the total 'real' solvation free energies.

Uncertainty and future work

It is very difficult to rigorously estimate error bars for these values because the data is so highly correlated and we have such short trajectories. The error bars should therefore be considered highly approximate as they are mainly determined from the difference between the direct and inverse forms of the PDT formula. There is obviously also the unquantifiable error that arises from assuming that revPBE-D3 structures are accurate. The neglect of

Table 4: Contributions to solvation free energies estimated using the direct and inverse formulations of the PDT for lithium in units of kJ mol^{-1}.

Contribution	Direct	Inverse	Final
μ^*_{Cav}[a]	5.08 to 5.50	—	5.29
$\mu^*_{\text{PC(0)}}$	−24.49	−21.95	−23.22
$\Delta\mu^*_{\text{Ew}}(0.1)$[b]	−42.05	−40.40	-41.22
$\Delta\mu^*_{\text{Ew}}(0.2)$	−51.32	−52.41	-51.87
$\Delta\mu^*_{\text{Ew}}(0.3)$	−63.50	−60.73	-62.12
$\Delta\mu^*_{\text{Ew}}(0.4)$	−73.76	−75.56	-74.66
$\Delta\mu^*_{\text{Ew}}(0.5)$	−86.12	−85.74	-85.93
$\Delta\mu^*_{\text{Ew}}(0.6)$	−97.32	−99.39	-98.35
$\Delta\mu^*_{\text{Ew}}(0.7)$	−108.58	−106.76	-107.67
$\Delta\mu^*_{\text{Ew}}(0.8)$	−116.30	−115.72	-116.01
$\Delta\mu^*_{\text{Ew}}(0.9)$	−125.03	−126.44	-125.73
$\Delta\mu^*_{\text{Ew}}(1.0)$	−136.90	−135.86	-136.38
$\mu_{\text{Ew-Corr}}$[c]	—	—	3.71
$q\phi_D$	46.31	—	46.31
$q\phi_B$	329.69	—	329.69
$q\phi_C$	-27.98	—	—
$\mu^*_{\text{Ch-Ion}}$[d]	48.62	49.28	48.94
μ^*_{Relax}[a]	—	−7.61 to −10.40	−9.01
$\mu^*_{\text{Corr}}(24)$	—	—	−2.09
$\mu^*_{\text{QZ-Corr}}(4)$[e]	—	—	−1.02
$\mu^*_{\text{CCSD(T)-Corr}}(4)$[f]	—	—	−0.06

[a] Effective R_{Cav} = 2.07 to 2.12 Å

[b] μ^*_{Ew} is calculated using Ewald summation and $\Delta\mu^*_{\text{Ew}}(q) = \mu^*_{\text{Ew}}(q) - \mu^*_{\text{Ew}}(q - \Delta q)$

[c] Described in Ref. 1

[d] Free energy of replacing point charge with real ion

[e] Correction to counterpoise corrected quadrupole zeta basis sets with four waters.

[f] Correction to CCSD(T) calculated with four waters

Table 5: Contributions to solvation free energies estimated using the direct and inverse formulations of the PDT for fluoride in units of kJ mol^{-1}.

Contribution	Direct	Inverse	Average
$\mu_{\text{Cav}}^{*}{}^{a}$	13.39 to 13.80	—	13.60
$\mu_{\text{PC(0)}}^{*}$	−13.97	−16.80	−15.39
$\Delta\mu_{\text{Ew}}^{*}(0.05)$	16.89	16.89	16.89
$\Delta\mu_{\text{Ew}}^{*}(0.10)$	14.74	14.99	14.87
$\Delta\mu_{\text{Ew}}^{*}(0.15)$	12.69	12.27	12.48
$\Delta\mu_{\text{Ew}}^{*}(0.20)$	9.73	10.52	10.13
$\Delta\mu_{\text{Ew}}^{*}(0.25)$	7.82	7.72	7.77
$\Delta\mu_{\text{Ew}}^{*}(0.30)$	4.42	5.94	5.18
$\Delta\mu_{\text{Ew}}^{*}(0.35)$	2.73	0.60	1.67
$\Delta\mu_{\text{Ew}}^{*}(0.40)$	−2.60	−1.59	−2.10
$\Delta\mu_{\text{Ew}}^{*}(0.45)$	−4.72	−6.07	−5.39
$\Delta\mu_{\text{Ew}}^{*}(0.50)$	−9.33	−10.16	−9.75
$\Delta\mu_{\text{Ew}}^{*}(0.55)$	−13.57	−11.82	−12.70
$\Delta\mu_{\text{Ew}}^{*}(0.60)$	−15.38	−15.88	−15.63
$\Delta\mu_{\text{Ew}}^{*}(0.65)$	−18.89	−18.71	−18.80
$\Delta\mu_{\text{Ew}}^{*}(0.70)$	−22.20	−22.80	−22.50
$\Delta\mu_{\text{Ew}}^{*}(0.75)$	−25.78	−25.29	−25.54
$\Delta\mu_{\text{Ew}}^{*}(0.80)$	−28.34	−29.19	−28.77
$\Delta\mu_{\text{Ew}}^{*}(0.85)$	−31.92	−30.98	−31.45
$\Delta\mu_{\text{Ew}}^{*}(0.90)$	−33.75	−34.87	−34.31
$\Delta\mu_{\text{Ew}}^{*}(0.95)$	−37.36	−36.87	−37.11
$\Delta\mu_{\text{Ew}}^{*}(1.00)$	−39.59	−41.21	−40.40
$\mu_{\text{Ew-Corr}}$	—	—	5.72
$q\phi_{D}$	−46.31	—	−46.31
$q\phi_{B}$	−333.65	—	−333.65
$q\phi_{C}$	42.44	—	—
$\mu_{\text{BM1}}^{*}{}^{b}$	24.02	21.78	22.90
$\mu_{\text{BM2}}^{*}{}^{b}$			21.01
$\mu_{\text{BM3}}^{*}{}^{b}$	38.85	39.75	39.30
$\mu_{\text{ChBM-Ion}}^{*}$	9.43	9.57	9.50
$\mu_{\text{Relax}}^{*}{}^{a}$	—	−7.11 to −8.61	−7.86
$\mu_{\text{Corr}}^{*}(24)$	—	—	37.19
$\mu_{\text{QZ-Corr}}^{*}(4)$	—	—	−2.64
$\mu_{\text{CCSD(T)-Corr}}^{*}(4)$	—	—	−2.78

[a] Effective R_{Cav} = 2.69 to 2.71 Å^{a}

[b] Free energy of inserting Born-Mayer repulsion. b = 2.338, A =237.5, 475 and 950 (a.u.)

quantum nuclear effects is an issue that should also be addressed in future. Path integral simulations with a classical water model[4] indicate that this effect may be on the order of 4 kJ mol^{-1}. This is similar in size to the uncertainty in the estimates reported here. Surprisingly this correction is positive for lithium and negative for fluoride, resulting in a much smaller correction for the salt value.

Improving the estimate of the μ^*_{Corr} correction will be important to test the values determined here. In particular, the CCSD(T) level of theory should be combined with larger basis sets and larger cluster sizes. The calculation of the surface potential of the air-water interface relies on GGA functionals.[2] This estimate appears robust and does not depend on functional, basis set or system size.[1] However, it is not possible to easily determine the error associated with DFT for this term, as it depends on the water structure. An improved level of theory could therefore lead to a different value, which would change the cation-anion split reported here. This would not change the experimental agreement however as this term makes compensating contributions for the cation and the anion. Performing sampling at the RI-MP2 level is therefore an important goal.

In future the method should be generalized to other ions such as water's self ions, potassium, sodium, cesium, iodide, divalent ions, tetra-phenyl arsonium and tetra-phenyl borate. SAPT should be used to rigorously partition the quantum mechanical energy into dispersion, exchange, and induction terms. The MP2 correction for ion-ion and ion-surface PMFs should be estimated. Finally, coarse grained models should be fit to reproduce the contributions so that more complex systems can be modeled cheaply.

References

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