

Electronic Structure and Stability of Benzene Radical Anion in Solution

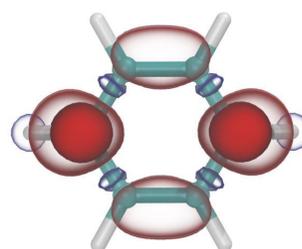
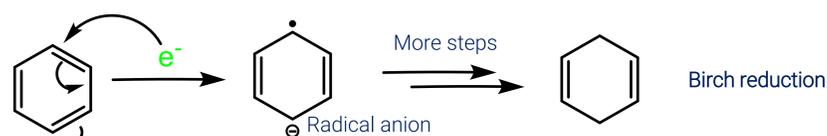
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Introduction

- The **radical anion of benzene** is formed in the initial stage of the **Birch reduction** of benzene. Here, a solvated electron [1], generated by dissolution of an alkali metal in liquid ammonia, attaches to neutral benzene forming the radical anion that is further reduced to 1,4-cyclohexadiene.
- The anion possesses many interesting physical properties too: notably, it is experimentally found to be a **short-lived metastable resonance in the gas phase** [2] but seems to be **long-lived enough to be measurable in the condensed phase** where spectroscopic experiments are performed [3].
- Our previous *ab initio* molecular dynamics (AIMD) simulations [4] of the species in explicit bulk liquid ammonia show a **localization** of the density corresponding to the excess electron (*i.e.*, spin density) on the molecule, **suggestive of a bound state**.
- In this follow-up work, we ask the explicit question “Does the benzene radical become bound in solution and can we estimate how much?” and answer it using **GW approximation** calculations of the electronic density of states (EDOS) as the individual one-electron energies averaged over the thermal ensemble from AIMD.



Spin density of the benzene radical anion (positive deviations in red, negative in blue) at the hybrid DFT level of theory. Note that compared to the traditional organic notation it is much more delocalized and complex.

Theory: why GW?

- Kohn-Sham density functional theory (KS DFT)** is a practical DFT formulation used for AIMD that is based on auxiliary non-interacting one-electron states in a fictitious KS potential. It gives access to the correct electron density and total energy but, unfortunately, does not provide physically meaningful one-electron energies.

$$(\hat{T} + \hat{V}_{\text{KS}})|\phi_n\rangle = \varepsilon_n^{\text{KS}}|\phi_n\rangle$$

- GW approximation** is a self-consistent electronic structure method that provides physical electron attachment/detachment energies and corresponding Dyson states based on the Green's function G, screened Coulomb potential W and self-energy Σ .

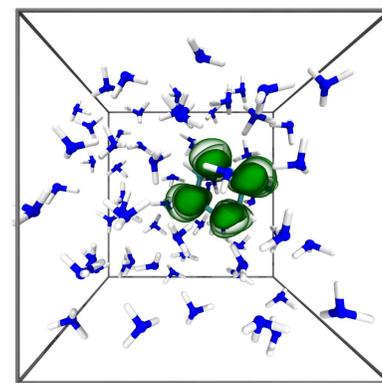
$$\Sigma = iGW$$

- G_0W_0 is a non-iterative flavor of GW that offers only a **correction to the unphysical KS one-electron energy eigenvalues** starting from the original set of KS states (that remain unchanged themselves) and exchange-correlation part of the KS potential.

$$\varepsilon_n^{G_0W_0} = \varepsilon_n^{\text{KS}} + Z_n \langle \phi_n | \Sigma(\varepsilon_n^{\text{KS}}) - V_{\text{XC}} | \phi_n \rangle$$

Computational Details

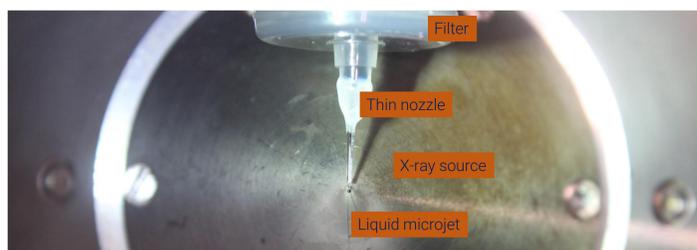
- Computational cost of GW scales as $O(N^4)$ and memory requirements as $O(N^3)$.
- Very costly** calculation for extended condensed phase periodic systems.
- G_0W_0 energies were calculated on **200 configurations for both systems** (the solvated radical anion and the neutral reference) using a revPBE0-D3/TZV2P level wavefunction and GTH pseudopotentials in CP2K 7.1 software.
- Total cost of production calculations was over **400,000 core-hours**.
- Jobs were parallelized over **16 or 8 compute nodes**, for the two systems, respectively, on the Salomon cluster.



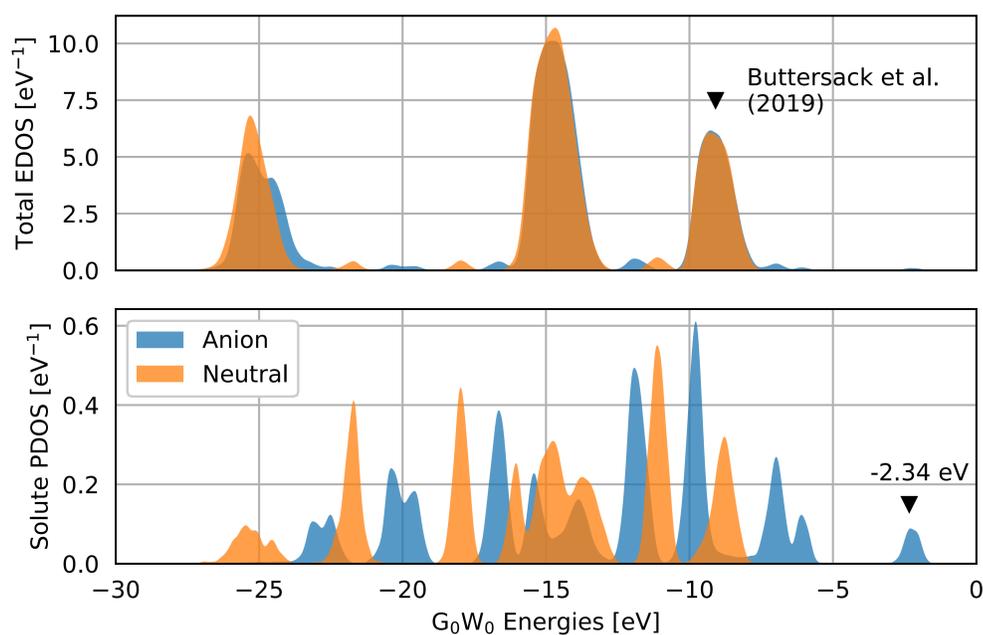
AIMD PBC box: positive parts of the localized spin density shown in green.

Results and Outlook

- Total EDOS of occupied states of the neutral and anionic solvated systems is shown in the top panel of the figure to the right.
- Total EDOS shows a **structure like the one observed before for neat ammonia** [5] with **additional low intensity features** due to the presence of the solute.
- Projection of the total EDOS on a localized basis allows to construct **projected density of states (PDOS)** that is used to decompose the total EDOS to molecular contributions.
- The anion solute PDOS clearly shows the excess electron to be **bound at -2.34 eV**.
- Anion solute PDOS shows spectrum that is **systematically less bound**: this might simplify experimental identification of species in realistic systems with chemical equilibria including solvated electrons and neutral benzene.
- Our experimental team has developed a **cryogenic microjet technique** [5] to measure **X-ray photoelectron spectra** of cold and volatile solutions that will provide equivalent experimental information to compare with our present theoretical predictions.



Calculated Density of States



Conclusion

- Our GW calculations clearly show **that the anion represents a bound system in solution**.
- Since GW gives access not only to the highest occupied state energy but to the whole spectrum, we predict **the whole electronic structure**.
- Projection** of the calculated density of states allows for disentanglement of the spectrum to **molecular contributions** without the need to perform a subtraction of reference spectra which is potentially problematic.
- Our computational prediction has implications for future XPS measurements that are scheduled for 2021 at the BESSY II synchrotron (Berlin, Germany).

[1] Buttersack T. et al. *Science* 2020

[2] Sanche L. Schulz G. J. *J. Chem. Phys.* 58, 1973

[3] Moore J. et al. *J. Phys. Chem.* 85, 1981

[4] Brezina K., Jungwirth P. and Marsalek O. *J. Phys. Chem. Lett.* 2020

[5] Buttersack T. et al. *J. Am. Chem. Soc.* 2019

