Structure and spectroscopy of the hydrated electron: Polarizable QM/MM simulations

John M. Herbert,[1] Leif D. Jacobson
[1] *The Ohio State University, Columbus, OH, USA*

A new one-electron model for finite water cluster anions, $(H_2O)_n^-$, and the bulk aqueous electron, e_{aq}^-, has been developed, based upon a reconsideration of the electron–water pseudopotential using *ab initio* quantum chemistry. The new model employs a polarizable force field for water, and both water–water polarization and electron–water polarization interactions are treated in a fully self-consistent manner. Although not fit directly to any observables, the model is quite accurate (as compared to various *ab initio* benchmarks) for small and medium-size $(H_2O)_n^-$ clusters, and also affords reasonable estimates of known experimental observables for e_{aq}^- in bulk water. We consider this to be the first hydrated-electron model that achieves at least semi-quantitative accuracy all the way from $n = 2$ to $n = \infty$. In the bulk, we find that self-consistent treatment of many-body polarization is qualitatively necessary in order to explain the gross features of the optical absorption spectrum of e_{aq}^-. In particular, the new model predicts the existence of polarization-bound, quasi-continuum states that are absent in non-polarizable models. These states are responsible for the "blue tails" that are consistently observed in optical spectra of e_{aq}^-, but which have not previously been seen in simulations. The implications of these results will be discussed, both in terms of our understanding of hydrated electrons and also in terms of future development of QM/MM methodology.