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A Perspective on "Volume and heat of hydration of ions"

Born M (1920) Z Phys 1: 45

B.M. Pettitt

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

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Abstract. Born's simple derivation of the free energy of hydration of ions is classic. It connects the microscopic atomic properties with the macroscopic thermodynamics in a transparent fashion.

Key words: Free energy – Poisson–Boltzmann – Solvation

Born's paper [1] in the first volume of *Zeitschrift für Physik* holds importance in many regards for my thoughts on the subject of hydration and the way in which many solvation calculations, new and routine, are now performed. The subject of calculating the thermodynamics, and in particular the free energies of hydration for species in aqueous solution, owes much to this rather brief (only three pages) work of Born. Whether by thermodynamic integration, thermodynamic perturbation or by a dressed quantum mechanical calculation, modern attempts to calculate equilibrium solvation effects are common in the literature [2–4]. Solvation effects are now often calculated for molecules as complicated as peptides and oligonucleotides in efforts to correlate experimental observations with our current understanding of the various phenomenological components of hydration [5].

With this work Born took the step of using atomic concepts and parameters, mixing them with continuum ideas (implicit solvent models) to make correlations with bulk thermodynamics. Not only was this a successful calculation but it remains a common theme in much current work on the subject some 80 years later. Born's theoretical understanding still underpins the field today, whether approached by many-body approximations [6] or by computer simulations [7].

Born's work on this paper evidently began when he read a pair of articles in which Fajans [8] had attempted to calculate the Born-cycle component of the work or free energy (there is some confusion in the works of the time using the words energy and free energy somewhat indiscriminantly as there is even today on occasion) for taking ions from an aqueous salt solution to a vacuum by using lattice energies calculated earlier by Born [9]. The calculations were regarded with some doubt by Born because of the need for ionization energies and electron affinities which were not available at the time. This produced "heats" with the wrong sign. Indeed Fajans had used hydrogen at a platinum electrode as a reference and in his first paper had omitted the "heat of evaporation of the electrons from the platinum" or the ionization energy. Even with an ad hoc correction, the calculation's accuracy still did not impress Born.

Born was, however, taken with the fundamental idea Fajans had about the process of hydration. Fajans recognized that the polarization of water in the presence of an ion and not the formation of stoichiometric hydrates was the dominating characteristic of ionic hydration. The idea that the dipole moment of water in proximity to the ions would be partially aligned was noted in the writings of Fajans [8] and Born [1]. Born utilized the concept of Nernst, by then familiar, that the dissolution of salts is correlated with solvent dielectric or solvent polarity. Born sought to quantify the idea.

Born then decided to neglect the explicitly detailed structure of water molecules and replace them with a continuous electrically polarizable medium. This approximation is the same as that made in any Poisson–Boltzmann calculation, but unlike the Debye–Hückel approximation, the ions in Born's calculation retained finite size. Thus, the Born treatment had the possibility of seeing chemically relevant differences due to ionic size. It should be remarked that Fajans was also looking for the chemically interesting dependence on ionic size in his less successful calculations.

Utilizing the relation between the integral of the field strength squared and the energy in the field, Born simply set the field contribution on the interior of ions to zero by integrating from the ionic radius to infinity. Subtracting the result in water (or any dielectric ε) from the result in air ($\varepsilon = 1$) gave his famous equation for the work of charging an ion in a dielectric continuum.

$$W = \frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right)\frac{z^2 e^2}{r_i}$$

From this, Born fit r_i to the experimental numbers for W. He was able to deduce that reasonable numbers for the ionic radii could be found. In addition, he found that the numbers for the positive ions were universally smaller than the then accepted atomic values (from crystal densities) and those for the anions were bigger. This he correctly interpreted in terms of the size change of the atom with the state of ionization long before the quantum mechanics of such systems was worked out.

This simple calculation, of which Born was quite skeptical, was the beginning of a quantitative understanding of ionic solutions in terms of atomic parameters. This would not be significantly improved in a systematic way until the work of Mayer in 1950 [10]. Building upon Mayer, Freidman [11] in the 1960s followed by a flood of researchers succeeded in increasing the level of correlations in the solution and the details of molecular structure in the solvent. With the rediscovery of finite-difference calculation methods for differential equations, the popularity of Born's method utilizing the Poisson–Boltzmann equation for irregularly shaped objects has allowed the extension of the method to large proteins and nucleic acids [12] in dilute saline solution. Theories to bring such macromolecular system calculations up to the level of Mayer have been in progress for the last decade or more.

Born's short paper brought the best ideas of the time together. It produced a work of lasting significance in terms of the ideas and concepts. Born first took the step of connecting atomic ideas with simple solvent field models to calculate bulk thermodynamics. It is still often cited as a fundamental intellectual source for ionic hydration theories and therefore must rank as one of the seminal contributions to theoretical chemistry in the twentieth century.

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