Radiative corrections for the hydrogen molecular ion HD^+

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In a recent accurate calculation of the vibrational-rotational energies of HD^+ by Wolniewicz and Poll[1] (WP), they emphasized the desirability of more detailed calculations of the radiative corrections for this molecular ion. They, themselves, estimated these corrections by assuming that radiative effects change the potential energy by

$$\Delta E^{\rm rad}(R) = \Delta E^{\rm rad}(\infty) + aR^{-1} + bR^{-2} + cR^{-3} ,$$

where R is the internuclear distance, and $\Delta E^{\rm rad}(\infty) = 0.272$ cm^{-1} is the radiative correction for the hydrogen atom. They then used our values of the radiative corrections to the vibrational energy levels $\Delta E_v^{\rm rad}$ of H_2^+ and[2] expectation values of R^{-1}, R^{-2}, and R^{-3} to obtain optimum values of a, b, and c. With these parameters fixed and expectation values of R^{-n} for HD^+ they calculated $\Delta E_v^{\rm rad}$ for HD^+. For $v > 10$ they used a slightly different formula which extrapolated to the correct asymptotic value.

In this Note we report a more direct calculation of $\Delta E_v^{\rm rad}$ which verifies the values determined by WP and answers their call for more detailed calculations. We use the same method as we did for the H_2^+ corrections[2]; namely, we correct the adiabatic-relativistic potential curve of HD^+ (using data from Refs. 3 and 4) by

$$E^{\rm rad}(R) = 0.2272[9.781 - \ln(k_0/\text{hartree})]\rho(R) \text{ cm}^{-1} ,$$

where $\rho(R)$ is the absolute value of the electron density at the nucleus and $\ln(k_0/\text{hartree})$ is the Bethe logarithm (for which we take the value 2.35[2]). Using the corrected and the uncorrected curves we calculate, by the Numerov–Cooley method, the vibrational energies and hence, from the differences, the values of $\Delta E_v^{\rm rad}$. These, with those of Ref. 1 are given in Table I. It is apparent that there is no substantial difference between these two sets of results and fears that inaccuracies may exist in the corrections given by WP may be laid to rest. The slight divergence for high vibrational levels is due to the fact that WP extrapolated to the exact asymptotic value for $v > 10$.

TABLE I. Radiative energy corrections for the vibrational levels of HD^+ in cm^{-1}.

v	$\Delta E_v^{\rm rad}$ (Ref. 1)	$\Delta E_v^{\rm rad}$ (This work)
0	0.351	0.350
1	0.342	0.342
2	0.335	0.335
3	0.328	0.328
4	0.321	0.321
5	0.315	0.315
6	0.310	0.309
7	0.305	0.304
8	0.300	0.299
9	0.295	0.295
10	0.291	0.291
11	0.287	0.287
12	0.284	0.284
13	0.281	0.281
14	0.279	0.278
15	0.277	0.276
16	0.275	0.273
17	0.274	0.272

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Lattice gas model of the ionic diffuse double layer[a)]

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The ionic diffuse double layer (DDL) plays an important role in the electrical behavior of solid and liquid electrochemical systems, colloids, and living cells. Three recent reviews[1–3] emphasize, however, that the conventional Gouy–Chapman[4,5] theory of the DDL breaks down even for concentrations well below 1 M. Stimulated perhaps by this lack of an adequate theory of a basic and widespread phenomenon, numerous complicated DDL theories (reviewed in Refs. 3, 6 and 7) have appeared in recent years. These theories, which involve a planar electrode, are mathematically very complex and often involve coupled nonlinear integral

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equations. Further, Reeves[1] has stated, "The collection of corrections to GCS (Gouy–Chapman–Stern) theory to be found in the literature are most unhelpful to the practicing electrochemist..."

It thus appears worthwhile to present a much simpler theory of the DDL, a liquid lattice gas model (LLGM), which should be applicable up to 1 M and beyond, and for potential differences across the DDL ψ_d from zero to many times the thermal potential $V_T \equiv kT/e$. The applicability of the theory will be evaluated by comparison to recent Monte Carlo (MC) results[6] for the primitive model of an aqueous electrolyte. This model involves a collection of positive and negative spherical ions of diameter d in an aqueous solution which is described entirely by the unsaturated dielectric constant of bulk water $\epsilon_B = 78.5$ at 298 K. Most of the complex DDL theories currently available deal only with this model. The conventional GCS [or modified Gouy–Chapman (MGC)] model involves a continuum treatment of point charges, an ideal gas approach. The present model considers spherical ions on a three-dimensional lattice of site concentration N. This model is theoretically completely applicable only for single crystals but yields surprisingly good results for liquids when a mean field correction[8,9] is added to it.

The lattice gas model was first developed for charges in solids and liquids by Grimley.[10] It has been applied recently[11] in considerable detail to such materials as AgCl, and the addition of mean field corrections to the model has also been considered.[8,9,12] Here we are concerned only with the LLGM, a model which assumes that a given lattice site may be empty (filled with water) or occupied by a negative or positive ion, concentrations n_1 or n_2, respectively.

The contribution to G/kT, the normalized free energy per unit volume, arising from the mean field approximation is $\alpha[(n_1^2/2N) + (n_2^2/2N) - (n_1 n_2/N)]$, where α is a normalized pair interaction energy, taken the same except for sign for like-sign pairs and unlike-sign ones, and taken positive for repulsion between like-sign pairs. When this contribution is included in the LLGM free energy,[11] one obtains[8,9]

$$\rho^* = -2\delta \sinh(\phi_1)/[(1-2\delta) + 2\delta\cosh(\phi_1)], \quad (1)$$

where $\phi_1 \equiv \phi + \alpha\rho^*$ and $\delta \equiv c_0/N$. Here $\rho^* \equiv \rho/eN$ is the normalized local charge density; $\phi \equiv \psi/V_T$, where ψ is the local potential referred to zero in the far bulk; and δ is the fractional bulk concentration of positive or negative charge ($n_1 = n_2 \equiv c_0$ in the bulk). Finally, the total charge in the diffuse layer σ_d is given in normalized form by[11,13]

$$Q_d \equiv \sigma_d/\sigma_n = -\operatorname{sgn}(\phi_d)\left[\left(\delta^{-1}\left|\int_0^{\phi_d}\rho^*(\phi)\,d\phi\right|\right)\right]^{1/2}, \quad (2)$$

where $\sigma_n \equiv V_T C_d \equiv 2ec_0 L_D$, $C_d \equiv \epsilon_B/4\pi L_D$, and L_D is the Debye length. The integral can be carried out exactly[11,13] when $\alpha = 0$, and when $\delta \to 0$ as well, it yields the usual GC result, $Q_d = -2\sinh(\phi_d/2)$. Here ϕ_d is the total normalized P.D. across the diffuse layer (not including the charge-free Stern layer). In the present case of interest $\alpha \neq 0$ and the implicit nonlinear Eq. (1) for ρ^* must be solved by iteration for each value of the integrand in Eq. (2). It has been found simplest to solve Eq. (1) in the transformed version $F(W) = A\sinh(\theta) + \sinh(W) = 0$, where $A \equiv 2\delta/(1-2\delta)$, $W \equiv \tanh^{-1}(\rho^*)$, and $\theta \equiv \phi + W + \alpha\tanh(W)$.

In the LLGM, $N = \sqrt{2}/D^3$, obtained from FCC packing of spheres of diameter D. Then $\delta \cong 4.26\times10^{-4} D^3 M$, where M is the molar concentration, D is in Å, and initially I take $D = d$. The present Q_d is related to the normalized σ_d, σ^*, used previously[6] by $Q_d = e\sigma_n d^{-2}\sigma^*$, equal to $15.11 M^{-1/2}\sigma^*$ for the choice[6] $d = 4.25$ Å. Fitting the above theory to the $M = 1$ MC results yields the curves of Fig. 1. The $\alpha = -3$ curve agrees with the MC results everywhere within one standard deviation of the MC values, agreement over a far wider range than any other current theory can provide.

A negative value of α implies attraction between charges of like sign; further, the magnitude of α found here is very much smaller than that following from pairwise Coulomb interactions, even those involving the unsaturated $\epsilon_B = 78.5$ value.[9] But much of the Coulomb interaction has already been implicitly incorporated through the local satisfaction of Poisson's equation. The sign of α found suggests that it has been overcompensated by the MGC and $\alpha = 0$ LLG models. Thus, the negative α value needed to yield agreement with the MC results provides a residual attraction between charges of like sign to compensate for the excess repulsion inherent in the MGC and $\alpha = 0$ LLG theories. The curvature in the $\alpha = -3$ curve at high $|Q_d|$ arises from the approach to close packing.

With $D = d$, $\delta \cong 3.27\times10^{-3}$ and 3.27×10^{-4} for $M = 0.1$ and 0.01, respectively. Very good LLGM fits of all the MC results can be obtained if both α and δ are independently varied. Even with $\alpha = -3.4$ and $\delta = 3.27\times10^{-3}$ a

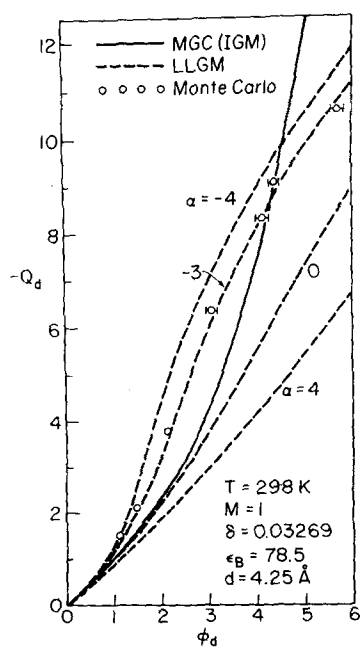

FIG. 1. The normalized diffuse double layer charge density vs the normalized potential difference across it. Monte Carlo, modified Gouy–Chapman (MGC), and liquid lattice gas model (LLGM) predictions are compared for a 1 m situation.

fairly good fit for 0.1 M is obtained. A comparable fit occurs with $\alpha = -3$ and $\delta = 5.2 \times 10^{-3}$, implying $D \cong 4.96$ Å. Again with $\alpha = -3$, the 0.01 M MC results are very well fitted with $\delta = 0.0016$, implying $D \cong 7.25$ Å. Since mean field theory suggests that α should be concentration independent, it is reassuring that good fits are possible here for 1 to 0.01 M with a constant α value. It is likely that the LLGM requires an increasing lattice step size with decreasing concentration because a fluid situation is being approximated by a lattice model. Finally, dielectric saturation can be readily added to the LLGM,[14] leading to a more realistic treatment. When MC results for both fluids and lattice situations become available it will be of interest to see how the LLGM α (and perhaps N as well) depends on d, ϵ_B, and M. The LLGM could then be of direct value to practicing electrochemists for both liquid and solid electrochemical applications since it would yield a much more accurate representation of DDL behavior than does conventional Gouy–Chapman theory.

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Classical time-correlation functions and the Lanczos algorithm[a]

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In recent years there has been a growing interest in the Lanczos algorithm[1] and its applications to problems in physics and chemical physics.[2] In particular, this algorithm was shown to be very useful in the calculation of correlation functions for slow motional ESR spectra.[3] Generally, in past work the computational value of this algorithm was emphasized. The Lanczos algorithm is not widely recognized as a theoretical method that can concisely extract the relevant information from a general description of physical systems.[4]

The value of the Lanczos algorithm to theoretical analyses derives from its close relation to the more general method of moments,[5] which may then be used in the study of the dynamics of classical statistical systems. One generally employs correlation functions to describe both the dynamical properties of a many particle system and the experimental data. We show here that the Lanczos algorithm leads in a natural way to their continued fraction representation.

Let us recall briefly the Lanczos algorithm. For a given self-adjoint operator $\mathbf{A}$, defined in a Hilbert space ϵ and given a normalized starting vector $|z\rangle \in \epsilon$, the method of moments[5] defines the nth approximation $\mathbf{A}_n$ of $\mathbf{A}$ by the relation

$$\mathbf{A}_n = \mathbf{P}_n \mathbf{A} \mathbf{P}_n \ , \tag{1}$$

where $\mathbf{P}_n$ is the operator that projects any vector belonging to ϵ, onto the subspace ϵ_n constructed with the vectors $|z_{k+1}\rangle = \mathbf{A}^k |z\rangle$ for $k = 0$ to $n-1$. If, by means of a Schmidt orthonormalization procedure, we produce an orthonormal basis set spanning ϵ_n represented by the vectors $|k\rangle$ for $k = 1$ to n, we obtain the recursion relation characteristic of the Lanczos algorithm[1,3(b)]

$$\beta_k |k\rangle = (\mathbf{A} - \alpha_{k-1} \mathbf{1}) |k-1\rangle - \beta^*_{k-1} |k-2\rangle \ . \tag{2}$$

A tridiagonal self-adjoint matrix $\mathbf{T}_n$, with the α_k's as diagonal elements ($\alpha_k \equiv \langle k | \mathbf{A}_n | k \rangle = \langle k | \mathbf{A} | k \rangle$) and the β_k's as off-diagonal elements ($\beta_k \equiv \langle k | \mathbf{A}_n | k-1 \rangle = \langle k | \mathbf{A} | k-1 \rangle$), constitutes the representation of $\mathbf{A}_n$ in this new basis set.

The application of the Lanczos algorithm to the calculation of the classical autocorrelation function (acf) is straightforward, once the acf is written as

$$F(t) \equiv \overline{f(t)^* f(0)} = \langle P_{eq}^{1/2} f | e^{-i\mathbf{L}t} | P_{eq}^{1/2} f \rangle \ , \tag{3}$$

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