

On the molecular theory of aqueous electrolyte solutions. III. A comparison between Born–Oppenheimer and McMillan–Mayer levels of description

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The utility of the McMillan–Mayer (MM) theory (applied at the pairwise additive level) for aqueous electrolyte solutions is examined by comparing with results previously obtained for a Born–Oppenheimer (BO) model. The structural properties and mean ionic activity coefficients calculated using both theoretical descriptions are compared for KCl, NaCl, and tetraalkylammonium bromide solutions. It is found that the success of the MM theory strongly depends upon the particular solution considered.

I. INTRODUCTION

As discussed by Friedman and Dale,¹ it is possible to consider electrolyte solutions on several theoretical levels. These range from the Schrödinger level (particles are electrons and nuclei) through the Born–Oppenheimer (BO) level (particles are solvent molecules and ions) to the McMillan–Mayer (MM) level (the only particles treated explicitly are the ions). The McMillan–Mayer approach² is based upon the notion that for many purposes it is not necessary to take explicit account of the solvent molecules in the theoretical formulation. Instead one considers the solution to be a fluid of ions with solvent effects included by replacing the true interionic interactions with solvent-averaged potentials of mean force. Although it is possible to formulate a general MM theory in terms of many-body solvent-averaged potentials,¹ in actual applications it is practical to include only the average pair potentials. The best known example of this approach is of course the so-called primitive model¹ which has been studied in great detail. The MM theory has been taken much further by Friedman and co-workers^{1,3} who have developed pair potentials which fit a wide range of experimental data for a number of aqueous electrolyte solutions.

However, despite its wide application in the theory of electrolytes, the MM description has never been tested against BO-level theory in a systematic self-consistent manner. The purpose of the present paper is to make such a comparison. This is made possible by the work described in Refs. 4 and 5 (i.e., papers I and II of this series) where we have solved the reference hypernetted-chain (RHNC) approximation for BO-level models for aqueous electrolyte solutions. For the model described in Ref. 4, results were obtained both at infinite dilution and at finite concentration for several alkali halide solutions. Hence it is a relatively simple matter to solve the HNC equations for fluids of ions (at finite concentration) interacting through the infinite dilution solvent-averaged potentials of mean force obtained for the molecular solvent model described in Ref. 4. Comparison of the results obtained in this manner with those given by the full BO-level calculations⁴ provides an unambiguous test of MM theory (applied at the pairwise additive level) for the model

solutions considered. We note that the theoretical approximations applied are also consistent since in the MM calculations the densities are sufficiently low for the HNC theory to be essentially exact for the hard sphere part of the ion–ion potentials. In the BO-level calculations the RHNC approximation ensures⁶ that the hard sphere interactions are treated correctly.

II. MODEL AND METHOD

The BO-level model considered in the present paper is described in Ref. 4. The solutions consist of charged hard sphere ions immersed in a solvent of hard spheres decorated with the polarizability, dipole moment, and quadrupole moment of the water molecule. The method of solution of the two component salt/solvent systems is discussed in Ref. 4 and it is not necessary to repeat the details here. The following is a brief summary of the MM-level calculations.

The solution of the RHNC equations for salt/solvent systems at infinite dilution yield^{4,5} solvent-averaged ion–ion potentials of mean force $w_{ij}(r)$. For the present model the potentials of mean force obtained can be expressed in the form

$$w_{ij}(r) = u_{ij}^{\text{HS}}(r) + \frac{q_i q_j}{\epsilon_0 r} + w'_{ij}(r), \quad (1)$$

where $u_{ij}^{\text{HS}}(r)$ is the usual hard sphere interaction, $q_i q_j / \epsilon_0 r$ is the long-range Coulombic term and $w'_{ij}(r)$ is a short-range contribution arising from the molecular nature of the solvent. We remark that for the present model the pure solvent dielectric constant ϵ_0 is 93.5 which is somewhat larger than the experimental value (i.e., 78.5) for water at 25 °C.

The MM results are obtained by solving the HNC theory for solutions of ions interacting via the potential (1). The equations which must be solved consist of the Ornstein–Zernike relationships expressed in the form

$$\tilde{\eta}_{ij}(k) = \sum_l \rho_l [\tilde{\eta}_{il}(k) + \tilde{c}_{il}(k)] \tilde{c}_{lj}(k) \quad (2)$$

subject to the closure conditions

$$c_{ij}(r) = -\eta_{ij}(r) - 1, \quad r < d_{ij}, \quad (3a)$$

$$c_{ij}(r) = \exp[\eta_{ij}(r) - \beta w_{ij}(r)] - \eta_{ij}(r) - 1, \quad r > d_{ij}, \quad (3b)$$

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where $\eta_{ij} = h_{ij} - c_{ij}$, h_{ij} , and c_{ij} are the pair and direct correlation functions, respectively, ρ_l is the number density of species l , $d_{ij} = (d_i + d_j)/2$, $\beta = 1/kT$, the tilde is used to denote Fourier transforms, and in Eq. (2) the sum on l is over all ionic species. We note that Eq. (3a) expresses the condition that for hard particles the radial distribution function, $g_{ij}(r) = h_{ij}(r) + 1$, must vanish if $r < d_{ij}$. Equations (2) and (3) were solved by iteration in the usual manner.⁴ The long-range Coulombic contributions to the pair and direct correlation functions were handled using the method of Springer *et al.*⁷

III. RESULTS AND DISCUSSION

The solvent parameters and ion diameters d_i used in the present calculations are summarized in Tables I and II of Ref. 4. It is helpful to recall here that the solvent diameter d_s was taken to be 2.8 Å and that the reduced ion diameters, $d_i^* = d_i/d_s$ used were 0.84, 1.08, 1.16, and 1.96 for Na⁺, K⁺, Cl⁻, Br⁻, and M⁺, respectively. We note that M⁺ is roughly similar in size to tetraalkylammonium ions. The BO-level calculations were carried out⁴ using experimental solution densities at 25 °C and 1 atm.

A. Ion-ion radial distribution functions

The K⁺/Cl⁻ and Cl⁻/Cl⁻ radial distribution functions obtained in KCl solutions ranging from 0 to 4 M ($M \equiv \text{mol L}^{-1}$) are shown in Figs. 1 and 2, respectively. We recall (cf., Refs. 4 and 5) that for the present (i.e., dipole tetrahedral-quadrupole) solvent model, ions of equal size and equal and opposite charge are solvated symmetrically such that $g_{++}(r) = g_{--}(r)$. Therefore, since K⁺ and Cl⁻ are of similar size the K⁺/K⁺ functions behave much like the Cl⁻/Cl⁻ results and hence the K⁺/K⁺ plots are not shown explicitly. It can be seen from Figs. 1(a) and 2(a) that at 0.025 and 0.1 M the MM- and BO-level results are in very good agreement. However, as the concentration is increased the discrepancies between the two theoretical levels become more important. For example, at higher concentrations [cf., Figs. 1(c)–1(d)] the characteristic oscillatory structure evident in the $g_{K^+Cl^-}(r)$ curves is more highly damped in the BO case. Also, as the concentration is increased to 4 M a shoulder and finally a peak develops at $(r - d_{ij})/d_s \sim 0.4$ in the BO results for $g_{Cl^-Cl^-}(r)$. This peak does not appear in the MM theory. Nevertheless, for KCl solutions the overall agreement between the MM and

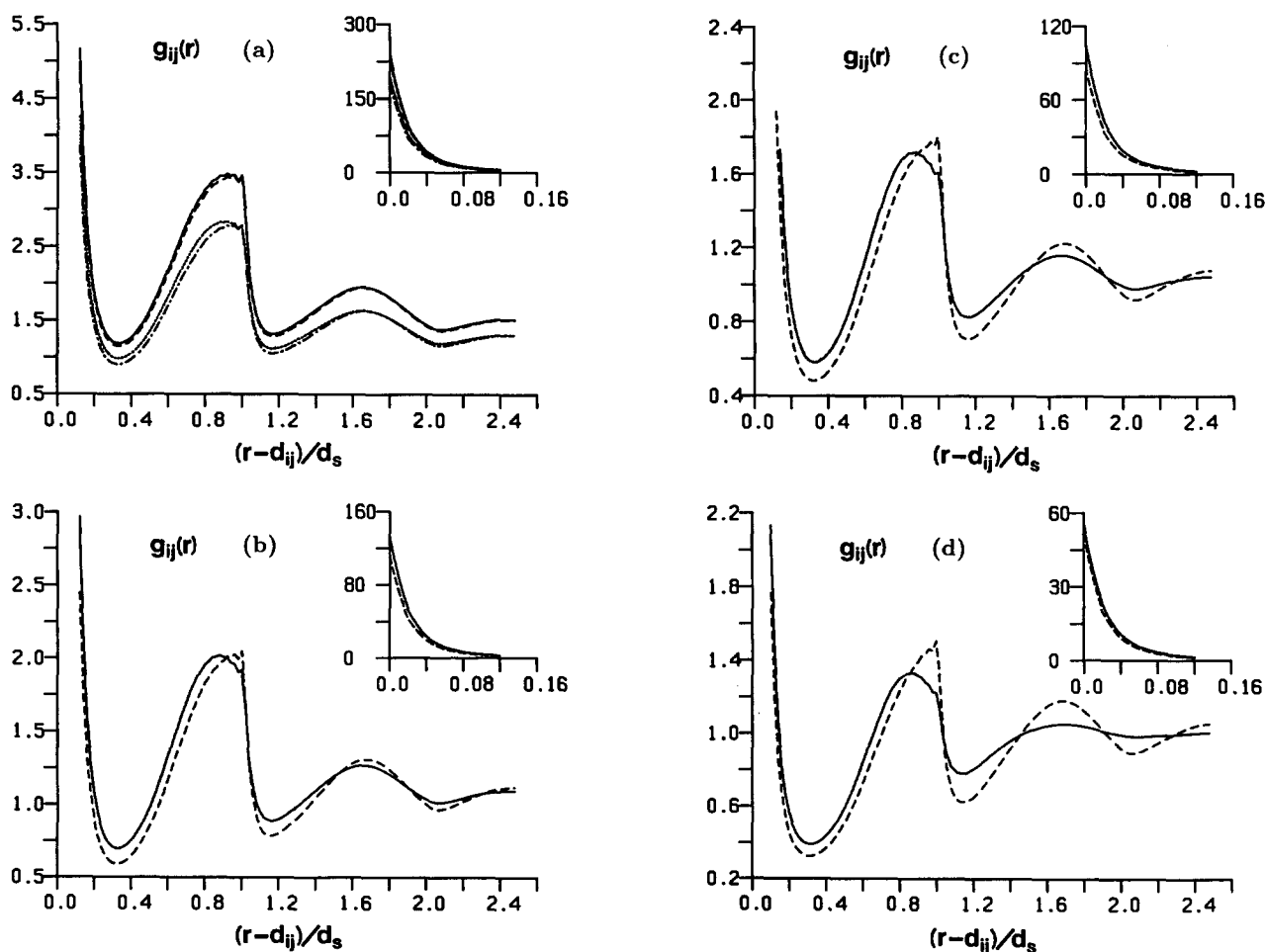


FIG. 1. The K⁺/Cl⁻ radial distribution functions obtained in KCl at (a) 0.025 and 0.1 M, (b) 0.5 M, (c) 1 M, and (d) 4 M. In figure (a) the solid and dotted curves are BO results at 0.025 and 0.1 M, respectively, and the dashed and dash-dot curves are the corresponding MM results. In figures (b)–(d) the solid and dashed curves represent the BO and MM results, respectively.

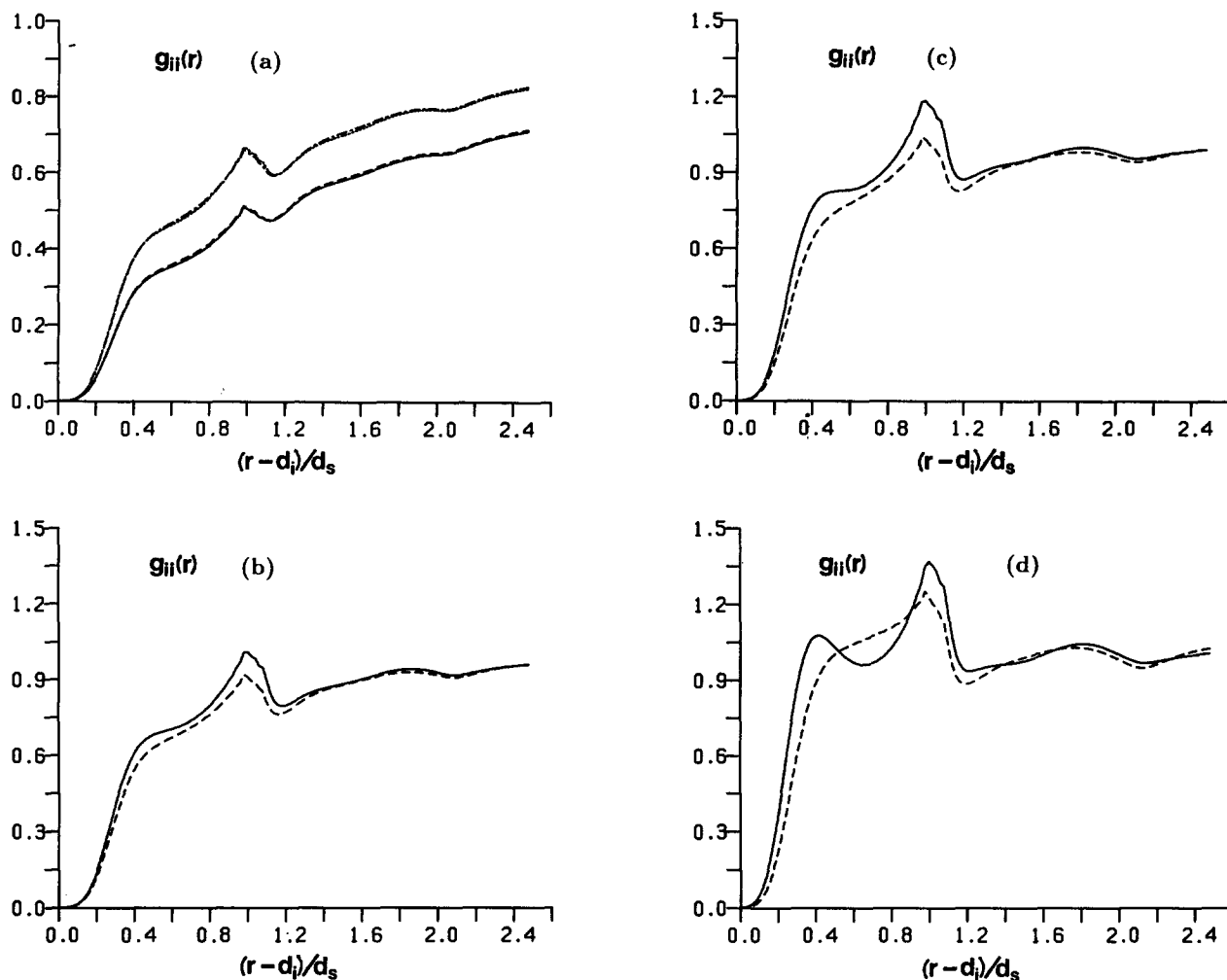


FIG. 2. The Cl^-/Cl^- radial distribution functions obtained in KCl at (a) 0.025 and 0.1 M, (b) 0.5 M, (c) 1 M, and (d) 4 M. The curves are as in Fig. 1.

BO levels of description is better than one might have expected particularly at concentrations as high as 4 M.

The NaCl systems differ dramatically from the KCl case in that we were unable to obtain solutions to Eqs. (2) and (3) (i.e., the MM-level equations) at concentrations much above 0.25 M. This contrasts with the BO-level equations which were easily solved⁴ at concentrations ranging up to 8 M. The $g_{\text{Na}^+\text{Cl}^-}(r)$ results are similar to the $g_{\text{K}^+\text{Cl}^-}(r)$ curves discussed above with the BO and MM results in good agreement at least for the low concentrations where numerical solutions were obtained. The 0.25 M curves are illustrated in Fig. 3. This is also true for $g_{\text{Cl}^-\text{Cl}^-}(r)$ at 0.025 and 0.1 M but, as shown in Fig. 4, significant differences occur at 0.25 M. This is particularly striking if we compare Fig. 4 with the 0.5 M KCl results given in Fig. 2(b).

For $g_{\text{Na}^+\text{Na}^+}(r)$ (cf. Figs. 5) the MM and BO level curves are in good agreement only at 0.025 M. The results begin to differ substantially at 0.1 M and the discrepancy is enormous at 0.25 M. We observe that unlike the situation for larger ions (e.g., K^+ , Cl^- , etc.) $g_{\text{Na}^+\text{Na}^+}(r)$ has a distinctive peak at $(r - d_i)/d_s \sim 0.4$. In the BO-level calculations it was found⁴ that the height of this peak decreased with increasing concentration for concentrations ≥ 0.1 M. In the

MM theory this tendency is reversed. The peak height increases rapidly as the concentration is increased leading to large discrepancies between MM and BO results as illustrated in Figs. 5(b)–5(c). Clearly, the concentration depend-

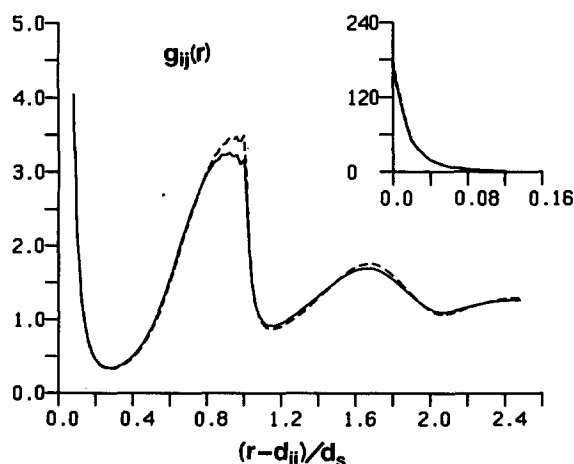


FIG. 3. The Na^+/Cl^- radial distribution functions obtained in NaCl at 0.25 M. The solid and dashed curves represent the BO and MM results, respectively.

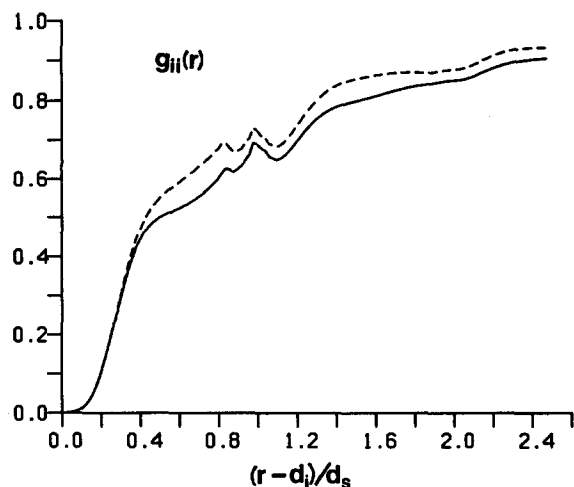


FIG. 4. The Cl^-/Cl^- radial distribution functions obtained in NaCl at 0.25 M. The curves are as in Fig. 3.

ence of the short-range peak must be crucially connected with ion-solvent interactions which are not adequately taken into account by the MM theory applied at the pairwise additive level.

The M^+/Br^- , Br^-/Br^- , and M^+/M^+ results obtained in MBr solutions ranging from 0.025 to 1 M are shown in Figs. 6–8. The agreement between the MM and BO calculations for $g_{\text{M}^+/\text{Br}^-}(r)$ is similar to that found for $g_{\text{K}^+/\text{Cl}^-}(r)$ at concentrations ≤ 1 M. We also note that the differences between the two levels of description do not grow rapidly as the concentration is increased from 0.5 to 1 M. For $g_{\text{Br}^-/\text{Br}^-}(r)$ the discrepancies between the theories tend to be a little larger than those observed for $g_{\text{Cl}^-/\text{Cl}^-}(r)$ in KCl solutions at the same concentration.

The M^+/M^+ curves shown in Figs. 8 are more interesting. As noted in Ref. 4, in the BO model $g_{\text{M}^+/\text{M}^+}(r)$ has a pronounced peak at $(r-d_i)/d_s \sim 0.2$. This peak is unlike the short-range peak found in $g_{\text{Na}^+/\text{Na}^+}(r)$ in that it occurs at a different position and, more importantly, it grows rather than decreasing in height as the concentration is increased. It is argued in Ref. 4 that the peak in $g_{\text{M}^+/\text{M}^+}(r)$ is due to hydrophobic effects which we would expect to be significant for large ions such as M^+ . Furthermore, we would also expect the relative importance of the hydrophobic attractions to increase as the Coulombic repulsions are screened and this is exactly what is observed. From Fig. 8 we see that in the MM theory the short-range peak also grows with increasing concentration but less rapidly than in the BO case. Consequently, at the higher concentrations the MM results lie substantially under the BO curves. This seems reasonable since we would expect the hydrophobic effects to be more important in the BO model where the solvent particles are explicitly included.

B. Activity coefficients

The MM and BO values obtained for $-\ln \gamma_{\pm}$ where γ_{\pm} is the mean ionic activity coefficient, are compared in Table I. These values were obtained by integrating the $(\partial \ln \gamma_{\pm} / \partial \rho_2)_{T,P}$ (ρ_2 is the salt concentration) results given

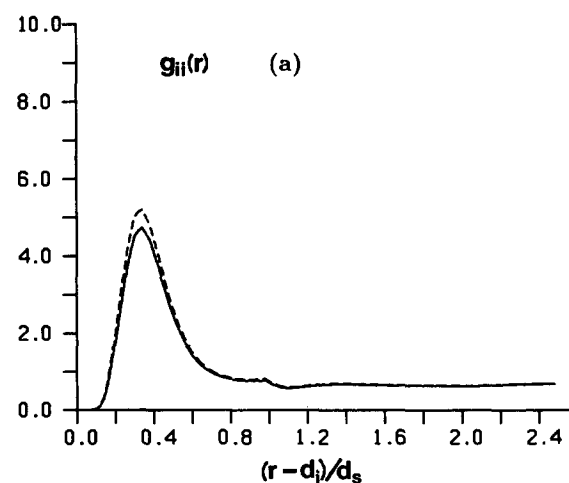
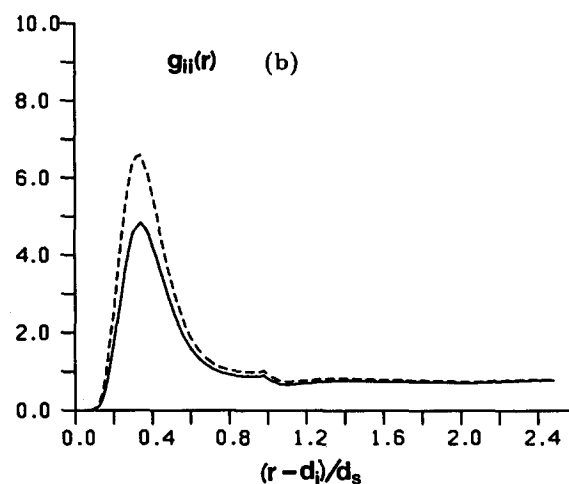
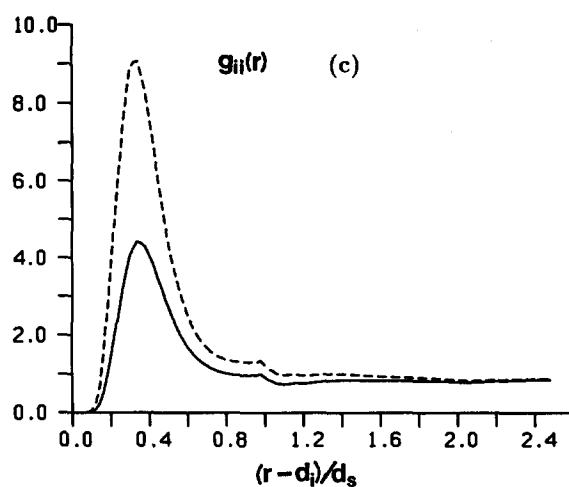


FIG. 5. The Na^+/Na^+ radial distribution functions obtained in NaCl at (a) 0.025 M, (b) 0.1 M, and (c) 0.25 M. The curves are as in Fig. 3.

by Kirkwood–Buff theory (cf. Refs. 4, 8, and 9). From Table I, it is apparent that for KCl solutions the MM and BO results are in surprisingly good agreement up to concentrations of 4 M. Indeed, the largest discrepancy between the two models at any concentration is only $\sim 2.5\%$. As discussed above, for NaCl MM results could not be obtained at concentrations above ~ 0.25 M. For NaCl solution at 0.25 M the MM result is $\sim 13\%$ larger in magnitude than the BO value.

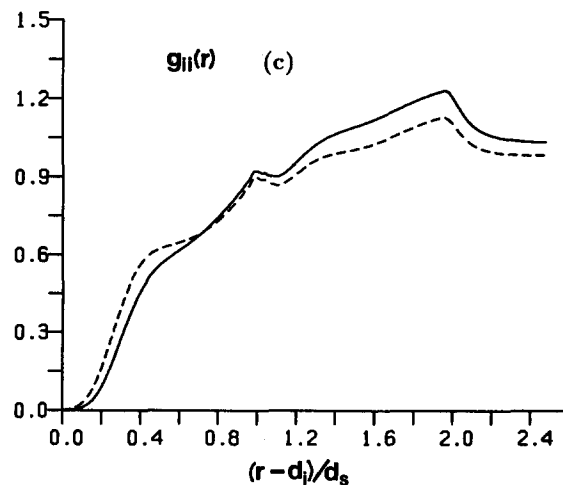
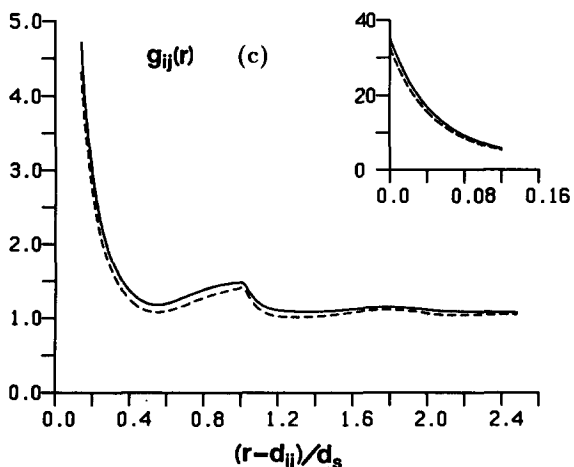
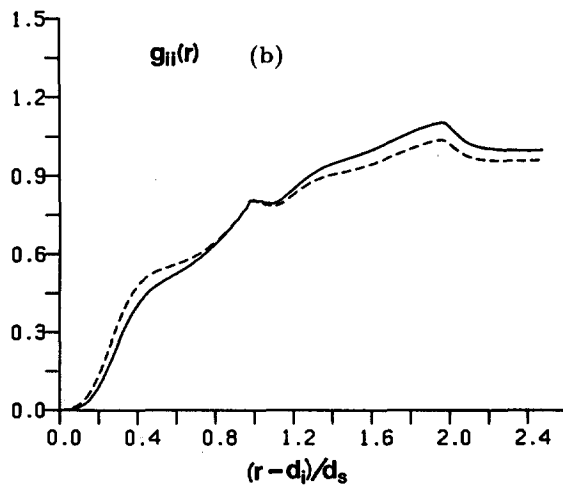
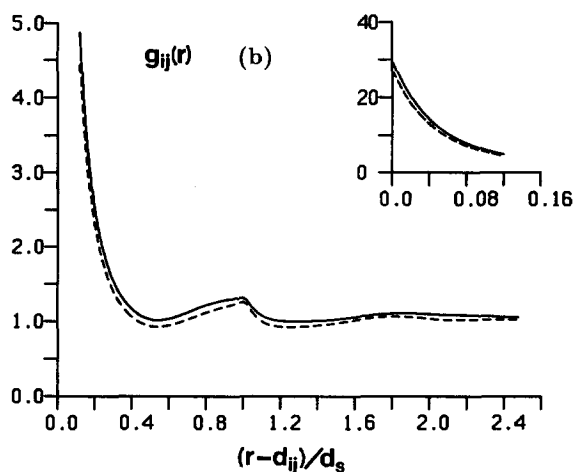
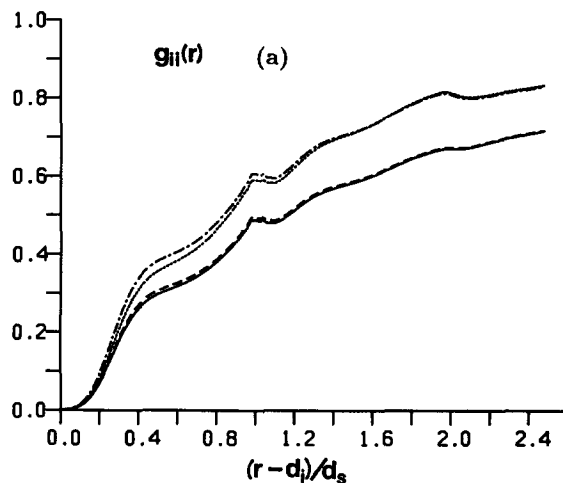
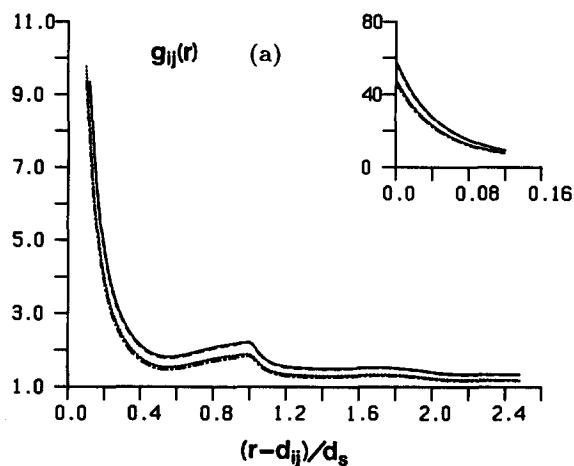


FIG. 6. The M^+/Br^- radial distribution functions obtained in MBr at (a) 0.025 and 0.1 M, (b) 0.5 M, and (c) 1 M. The curves are as in Fig. 1.

FIG. 7. The Br^-/Br^- radial distribution functions obtained in MBr at (a) 0.025 and 0.1 M, (b) 0.5 M, and (c) 1 M. The curves are as in Fig. 1.

For MBr solutions the MM and BO calculations are in good agreement at the lower concentrations but the MM results for $\ln \gamma_{\pm}$ fall less rapidly than the BO values as the concentration is increased. We note that at 1 M the MM and BO results for MBr solution differ by $\sim 20\%$.

IV. SUMMARY AND CONCLUSIONS

In this paper we have compared the Born–Oppenheimer and McMillan–Mayer descriptions of model aqueous electrolyte solutions. The MM theory was applied at the pair-

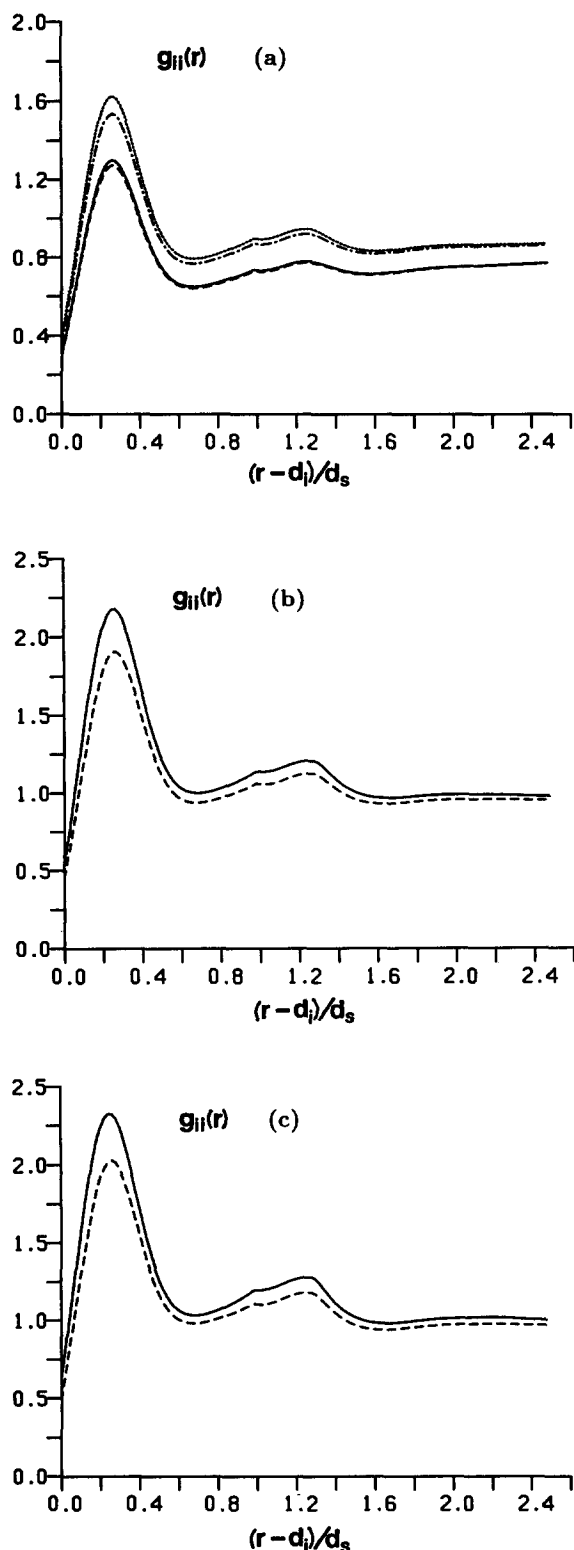


FIG. 8. The M^+/M^+ radial distribution functions obtained in MBr at (a) 0.025 and 0.1 M, (b) 0.5 M, and (c) 1 M. The curves are as in Fig. 1.

wise additive level and the calculations were carried out using the HNC theory. This is consistent with the earlier BO-level calculations for which the RHNC theory was employed.⁴ In the present paper KCl, NaCl, and MBr [e.g., $(C_2H_5)_4NBr$] solutions were considered.

It was shown that the utility of the pairwise additive MM-level description depends to a large extent upon the

TABLE I. The values of $-\ln \gamma_{\pm}$ obtained using MM and BO-level calculations. c is the concentration in mol l^{-1} .

c (M)	KCl		NaCl		MBr	
	BO	MM	BO	MM	BO	MM
0.025	0.142	0.142	0.141	0.142	0.143	0.145
0.1	0.279	0.280	0.275	0.288	0.291	0.297
0.25	0.425	0.426	0.430	0.486	0.482	0.468
0.50	0.573	0.570			0.722	0.650
1.0	0.759	0.744			1.085	0.889
2.0	0.977	0.952				
4.0	1.18	1.20				

particular electrolyte solution considered. For KCl and MBr solutions the MM and BO equations could be solved over comparable ranges of concentration and the ion-ion correlation functions given by the MM theory were in reasonably good agreement with the BO results for concentrations less than 1 M. Indeed for KCl the agreement remained fair up to 4 M. Also for KCl the mean ionic activity coefficients given by both levels of theory were in exceptionally good agreement at all concentrations up to 4 M. For MBr the discrepancies in $\ln \gamma_{\pm}$ were larger and increased with concentration reaching $\sim 20\%$ at 1 M. Nevertheless, for KCl and MBr solutions the MM theory is generally in good agreement with the BO results and the agreement extends to surprisingly high concentrations.

However, despite the relative success of the MM theory for KCl and MBr solutions it failed rather dramatically for the model NaCl solution considered. In fact, for NaCl solutions the HNC equations employed at the MM level could not be solved for concentrations in excess of ~ 0.25 M. This is in striking contrast to the BO case where RHNC results could be easily obtained up to 8 M. The source of this remarkable discrepancy was traced to the Na^+/Na^+ pair correlation function which behaves very differently in the BO and MM-level calculations.

Thus we conclude that although the pairwise additive MM theory can be used with some confidence (provided of course that the solvent-averaged ion-ion potentials of mean force at infinite dilution are known) for certain systems its success is likely to strongly depend upon the ionic species present and/or upon the model potentials employed. In particular the MM description is unlikely to be very reliable for solutions where relatively small ions such as Na^+ are present.

ACKNOWLEDGMENT

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