$$+ [2\, N_A^2\, N_B^2 - N_B^2] \sum_{ikl} (C_i^A\, C_k^B\, C_l^B\, V_{kl}(1)\; \varphi_i(1)/\varphi_A^0\,(1)) \;+ [2\, N_A^2\, N_B^2 - N_A^2] \sum_{ikl} (C_i^B\, C_k^A\, C_l^A\, V_{kl}(2)\; \varphi_i(2)/\varphi_B^0\,(2))$$

$$- [N_A^2\, N_B^2/2] \sum_{ijkl} C_i^A\, C_j^A\, C_k^B\, C_l^B\, V_{kl}(1)\; \varphi_i(1)\; \varphi_j^*(1)/|\,\varphi_A^0(1)\,|^2 +$$

$$- [N_A^2\, N_B^2/2] \sum_{ijkl} C_i^A\, C_j^A\, C_k^B\, C_l^B\, V_{ij}(2)\; \varphi_k(2)\; \varphi_l^*(2)/|\,\varphi_B^0(2)\,|^2,$$

where

$$V_{\alpha\beta}(i) = \int (\varphi_\alpha^*(j)\; \varphi_\beta(j))\; (1/r_{ij})\; \mathrm{d}v_j\,.$$

This HAMILTONIAN is exact (apart from exchange terms which can be included later) if Φ_0 is the product of one-electron pseudo-wave functions. *We suggest that the equation $H_{12}^M \Phi_0 = E\, \Phi_0$ is a good approximation also if Φ_0 is a correlated pair function.* This assumption is strongly supported by the following argument. The operator H_{12}^M is derived in such a way that the orthogonality projection operator $(1 - \Omega_{12})$ is transformed into pseudopotentials. But we orthogonalize correlated and uncorrelated two-electron functions with the same operator; i. e. $(1 - \Omega_{12})$ is the same regardless whether it operates on a correlated or uncorrelated function[2].

By transforming $(1 - \Omega_{12})$ we have eliminated the troublesome integrals from the calculations. By solving

$$H_{12}^M\, \Phi_0 = E\, \Phi_0$$

variationally we can put Φ_0 in a HYLLERAAS form and only two-electron integrals will occur since all terms in H_{12}^M have the character of potentials.

The method is developed here for the two valence electrons of an atom. Generalization for an arbitrary electron pair is straightforward. The wave function will be the same again with Φ representing any electron pair. The derivation of H_{12}^M will follow the same steps but the equations for φ_A^0 and φ_B^0 will be different and therefore also H_{12}^M will be slightly different.

As a first, demonstrative calculation we computed a correlated pair function for the (2s) shell of the Be atom. Since the pseudo-wave functions are not available for the Be (2s) electrons we used the pseudo-wave function for the (2s) electron of Be^+ ion[7]. It can be shown that the pseudopotentials are not sensitive to small changes in the pseudo-wave function[8]. Using a 6 term HYLLERAAS type function with a SLATER function as the leading term we obtained a correlation energy of $E_c = -0.0302$ a. u. By carrying out the orthogonalization explicitly one obtains with the same ansatz $E_c = -0.0321$ a. u.[5]. The agreement is very good; the small difference is probably a result of using Be^+ pseudopotentials instead of the correct ones for Be.

The work is being continued and the results will be presented in forthcoming publications.

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Proton Spin Relaxation in Paramagnetic Ion Solutions: Deuterium Isotope Effect

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In aqueous paramagnetic ion solutions the observed rate of proton spin relaxation $(1/T_2)$ is controlled by the rate of relaxation in the primary hydration shell of the paramagnetic ion $(1/T_{2x})$, and by the rate of proton exchange between the hydration shell and the solvent. The relaxation rate is given by

$$1/T_2 = P\,(T_{2x} + \tau_{xw})^{-1}\,, \qquad (1)$$

where P is the fraction of protons in hydration shells, and τ_{xw} is the mean lifetime of a proton in the hydration shell. The effects of isotopic substitution have been studied by measurement of deuteron spin relaxation in D_2O solutions[1, 2], and of proton and deuteron relaxation in solutions of mixed isotopic composition[3–6]. The present discussion will apply to cases like Cr^{3+} and VO^{2+}, where the dominant exchange mechanism is proton transfer across hydrogen bonds, rather than exchange of whole water molecules. We seek to account for changes in the T_2 of protons (and deuterons) with variation in the isotopic composition of the solution, as have been observed by MAZITOV and RIVKIND[5, 6].

If the solution contains a mixture of the isotopes H and D, the factor P in Eq. (1) is given by

$$P = (n\, x/w)\; (\beta_x/\beta_w)\,, \qquad (2)$$

where n is the hydration number, x is the paramagnetic ion concentration, w is the concentration of water molecules, and β is the fractional concentration of protons – i. e., $\beta_x = H_x/(H_x + D_x)$, and $\beta_w = H_w/(H_w + D_w)$. Due to the difference in zero-point vibrational energy, the chemical rate constants for H and D exchange dif-

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fer [7]. Since the H and D systems are separately in equilibrium we have the usual relationship between rate constants and concentrations – i. e., $k_{wx}{}^{\mathrm{H}}/k_{xw}{}^{\mathrm{H}} = H_w/H_x = K_{\mathrm{H}}$, and similarly for D. Using these relations to eliminate H_w and D_w from the defining expressions for the β's, we get homogeneous algebraic equations for H_x and D_x. The condition for a non-trivial solution requires that $\beta_w/\beta_x = (1-K)\,\beta_w + K$, where $K = K_{\mathrm{H}}/K_{\mathrm{D}}$. For a dilute solution β_w is very nearly the same as the overall proton fraction (β). Thus, Eq. (1) becomes

$$T_2{}^{\mathrm{H}} = (w/n\,x)\,(T_{2x}+\tau_{xw})_{\mathrm{H}}[(1-K)\,\beta+K]. \qquad (3)$$

The analogous expression for $T_2{}^{\mathrm{D}}$ is obtained by replacing K by K^{-1}, and β by $(1-\beta)$. The ratio of deuteron to proton relaxation times in the same solution comes out to be $T_2{}^{\mathrm{D}}/T_2{}^{\mathrm{H}} = (T_{2x}+\tau_{xw})_{\mathrm{D}}/K(T_{2x}+\tau_{xw})_{\mathrm{H}}$, which is not explicitly dependent on β. The ratio $K = K_{\mathrm{H}}/K_{\mathrm{D}}$ is temperature dependent — i. e.,

$$K = \exp(\Delta G_{\mathrm{D}} - \Delta G_{\mathrm{H}})/R\,T\,,$$

hence the isotope effect will be most pronounced at low temperature.

The experimental results of Mazitov and Rivkind [5, 6] are in partial agreement with the above conclusions. The observed relaxation times are either constant, or decrease linearly with β. For a 0.1 M solution of $\mathrm{CrNO_3}$, at 0 °C, both $T_2{}^{\mathrm{H}}$ and $T_1{}^{\mathrm{H}}$ data indicate $K = 2$. For a 0.16 M solution of $\mathrm{VOSO_4}$, at 25 °C, the $T_2{}^{\mathrm{H}}$ and $T_2{}^{\mathrm{D}}$ data are entirely compatible with the above picture, and give $K = 1.6$. On the other hand, $T_{1,2}{}^{\mathrm{D}}$ in the case of Cr^{3+}, and $T_1{}^{\mathrm{H,D}}$ in the case of VO^{2+} show at most slight variations with β, contrary to what would be expected from Eq. (3).

The above analysis is based on the assumption of a simple "primary" isotope effect. In contrast, the explanation offered by Mazitov [5] invokes a dependence of the lifetimes, $\tau_{xw}{}^{\mathrm{H,D}}$, upon isotopic composition of the solution. Such a dependence would be classed as a secondary isotope effect [7], and may well be required for a complete explanation of the experimental results. However, the data presently available do not really permit one to draw definitive conclusions along these lines. This is because recent work has shown that unless the concentrations of proton donors like $\mathrm{H_3O^+}$ and $\mathrm{HSO_4^-}$ are suitably adjusted, the relaxation behavior of the system lies outside the realm of validity of the simple Eq. (1) [8, 9]. Nevertheless, it seems clear that experimental studies of this kind will allow one to distinguish between primary and secondary isotope effects, as well as to make inferences regarding mechanisms of proton transfer reactions involving paramagnetic complex ions.

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Hydrogen Isotope Effect among the Different Dehydration Stages of $\mathrm{CuSO_4 \cdot 5\,H_2O}$

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Several investigations are reported in the literature dealing with the fractionation of hydrogen isotopes between salt hydrates and their saturated solutions. The measurements by Day et al. [1], Teis [2], and Uusitalo [3] showed either no isotope effect or an enrichment of deuterium in the solid phase. Barrer and Denny [4], however, found an inverse effect in several chloride and sulphate systems. Their result was a few per cent enrichment of the light isotope in the hydration water of the crystal. Based on the assumption that hydration effects in the crystal are similar to those of the ions in solution, their results are in agreement with calculations by Swain, Bader and Thornton [5], concluding that in solutions the hydration water of ions has a smaller D/H ratio than the bulk water. This conclusion has been supported in the case of the hydronium ion by NMR [6, 7] as well as by vapor pressure measurements [8].

Only one investigation is known searching for a difference in the D/H ratio of water liberated on stepwise dehydration of hydrated crystals. Anderson et al. [9] used water containing 0.5% $\mathrm{D_2O}$ for the hydration of anhydrous $\mathrm{CuSO_4}$ and found that on dehydration the first four molecules of water liberated were heavier than the fifth. The variations in their data, however, did not enable them to attach a quantitative significance to the results.

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