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Jerry Goodisman

University of Illinois at Urbana-Champaign

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equilibrium concentration data for the system investigated have been reported.³ The self-diffusion coefficients were calculated using the equation⁵

$$D_i = \frac{RT10^3 K \bar{l}_i}{|Z_i| F^2 \bar{C}_i} \quad (4)$$

where K is the specific conductance and $\bar{l}_i$ is the transport number of species i in the membrane. In the conductivity measurements $\bar{C}_i$ was constant across the membrane, i.e., $\bar{C}_i = \bar{C}_i'$. Providing that $\bar{l}_A = \bar{l}_B$ for conductance of ions A^+ and B^+ in the membrane and assuming that $\bar{C}_i = \bar{C}_i'$, substitution of eq 4 into eq 3 yields

$$J_a/J_b = K_a/K_b \quad (5)$$

The experimental fluxes obtained for multiionic interdiffusion are shown in columns 1 and 2 of Table I. Experimental flux ratios and flux ratios calculated using eq 5 are given in columns 3 and 4, respectively. For comparison, the ratio of ionic mobilities in H_2O are shown in column 5.

The provision that $\bar{C}_i = \bar{C}_i'$ for a static system applies to a dynamic system may not represent a true model for multiionic interdiffusion. Also, interactions between solute ions in multicomponent systems may be appreciable as demonstrated by Wendt.⁶ However, the relation between single-ion interdiffusion coefficients as determined from conductivity data and flux ratios calculated for multiionic systems does predict the observed trends in experimental flux ratios. Where the self-diffusion coefficients for the competitively diffusing ions are nearly the same, as for Na^+ and K^+ , the calculated values are in good agreement with experimental values.

The total flux for the multiionic systems decreases in the presence of Ca^{2+} and to a greater extent with Cu^{2+} . This trend is in agreement with the decrease in flux for biionic interdiffusion in the presence of Ca^{2+} and Cu^{2+} reported previously.³ The barrier properties of the membrane as altered by complexing ions not only cause a decrease in the total flux but also affect the relative fluxes of the competitively diffusing univalent ions. The flux ratios are observed to increase in the presence of Ca^{2+} and decrease in the presence of Cu^{2+} .

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Scaling in Carbon Monoxide and Nitrogen

by J. Goodisman

Department of Chemistry, University of Illinois, Urbana, Illinois
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In a recent article,¹ the possibility of scaling the electronic wave function for a molecule for use on a second molecule isoelectronic to the first was discussed. Calculations were made for the pairs H_2 - He_2^{2+} and LiF - BeO . It was pointed out that the accuracy of the energy and other expectation values obtained from the scaled function could throw some light on the similarities or differences between the two molecules involved, and it was noted that the pair CO - N_2 would be a good candidate for such calculations. At about the same time as ref 1, self-consistent field calculations were published by Huo² on CO and BF . Less extensive calculations on N_2 , CO , and BF have been published by Nesbet.³ We here report the results of scaling on these wave functions.

Briefly, the scaling method is as follows: let $\psi_1(r;R)$ be a normalized electronic wave function (within the Born-Oppenheimer approximation) for molecule I. The scaled wave function ψ_{1s} is obtained by multiplying all coordinates by the scaling factor s .

$$\psi_{1s} = s^{3n/2} \psi_1(sr; sR) \quad (1)$$

Here, $s^{3n/2}$ is the normalizing factor with n the number of electrons, r refers to all electronic coordinates, and R and sR refer to the coordinates of the nuclei, which enter as parameters. Specializing to diatomic molecules, let molecule II be related to molecule I by having the charge on nucleus A multiplied by Z_A and the charge on nucleus B multiplied by Z_B . Then, scaling a wave function obtained for molecule I and using this to calculate the expectation value of the Hamiltonian for molecule II, we have

$$\begin{aligned} \bar{E}_s(R) = & s^2 T_1(sR) + s C_1(sR) + s Z_A L_1^A(sR) + \\ & s Z_B L_1^B(sR) + s Z_A Z_B M_1(sR) \end{aligned} \quad (2)$$

where sR is the internuclear distance for molecule I and R is that for molecule II, $T_1(sR)$ is the expectation value of electronic kinetic energy, $C_1(sR)$ is the expectation value of interelectronic repulsion, $L_1^A(sR)$ is the expectation value of the interaction of electrons with nucleus A, $L_1^B(sR)$ is the expectation value of the

(1) J. Goodisman, *J. Phys. Chem.*, **69**, 2520 (1965).

(2) W. Huo, *J. Chem. Phys.*, **43**, 624 (1965).

(3) R. K. Nesbet, *ibid.*, **40**, 3619 (1964).

(5) K. S. Spiegel and C. D. Coryell, *J. Phys. Chem.*, **57**, 687 (1953).

(6) R. P. Wendt, *ibid.*, **69**, 1227 (1965).

interaction of electrons with nucleus B, and $M_1(sR)$ is the nucleus-nucleus potential energy. All expectation values are for the Hamiltonian of molecule I, at an internuclear distance of sR .

In accordance with the variation principle, the value of s which minimizes $\bar{E}_s(R)$ with sR held fixed at R_0 is

$$s_0 = -[2T_1(sR)]^{-1}[C_1(sR) + Z_A L_1^A(sR) + Z_B L_1^B(sR) + Z_A Z^B M_1(sR)] \quad (3)$$

With this value of s , $\bar{E}_s(R) = -s_0^2 T_1(sR)$, where $R = R_0/s_0$. Thus, if we know the expectation values in (3) for molecule I at internuclear distance R_0 , we can calculate an energy for molecule II at internuclear distance R_0/s_0 . In addition, if $f(r)$ is a function homogeneous of degree i in the electronic coordinates whose expectation value for molecule I at R_0 is $\langle f \rangle_1^{sR}$, its expectation value for molecule II at R_0/s_0 is

$$\langle f \rangle_s^R = \langle f \rangle_1^{sR}/s^i \quad (4)$$

For instance, the operators for the electronic contribution of the dipole and quadrupole moments are homogeneous of degrees 1 and 2, while the nuclear contribution is in each case exactly calculable before and after

Table I

A. Calculations for $N_2 \rightarrow CO$				
$R = R_{CO}$ (a_0)	$sR = R_{N_2}$ (a_0)	s	$\bar{E}_s(R)$, au	$Q^{CO}(R)$, 10^{-26} esu
1.9	1.744393	0.9181016	-108.77378	-2.35978
	1.868	0.9831579	-109.45037	-2.06478
	2.068	1.0884211	-108.66208	-1.69994
2.1	1.868	0.8895238	-108.15949	-2.52235
	2.068	0.9847619	-109.41979	-2.07666
	2.268	1.0800000	-108.76676	-1.73290
2.3	2.068	0.8991304	-108.28212	-2.49106
	2.268	0.9860870	-109.33383	-2.07868
	2.391607	1.0398291	-109.18303	-1.86499
B. Calculations for $CO \rightarrow N_2$				
$R = R_{N_2}$ (a_0)	$sR = R_{CO}$ (a_0)	s	$\bar{E}_s(R)$, au	$Q^{N_2}(R)$, 10^{-26} esu
1.9	1.808393	0.9517858	-106.33909	-1.54651
	1.932	1.0168421	-106.05240	-1.18271
	2.132	1.1221053	-103.61866	-0.61519
2.1	1.932	0.9200000	-106.04849	-1.44480
	2.132	1.0152381	-105.96874	-0.88990
	2.332	1.1104762	-103.88725	-0.45413
2.3	2.132	0.9269565	-105.96991	-1.06748
	2.332	1.0139130	-105.83591	-0.54476
	2.455607	1.0676552	-104.39311	-0.27038

Table II

A. Comparisons with calculated results for CO				
R_{CO}	E_{CO} (SCF)	E_{CO} (scaling)	Q_{CO} (SCF)	Q_{CO} (scaling)
1.8084	-112.66220		-2.02948	
1.9		-109.48065		-1.99651
1.932	-112.72952		-1.94022	
2.1		-109.44389		-2.01531
2.132	-112.75878		-1.79077	
2.3		-109.35349		-2.02154
2.332	-112.73211		-1.60514	
B. Comparisons with calculated results for N_2				
R_{N_2}	E_{N_2} (SCF)	E_{N_2} (scaling)	Q_{N_2} (SCF)	Q_{CO} (scaling)
1.868	-108.94320		-1.32522	
1.9		-106.35619		-1.47599
2.068	-108.97143		-1.19197	
2.1		-106.25835		-1.19933
2.268	-108.92938		-1.03270	
2.3		-106.11754		-0.83612
2.3916	-108.88528		-0.91728	

scaling. Choice of origin¹ may be important; for the quadrupole moment, we follow Nesbet² in maintaining the origin at $16/23$ the distance from the C to the O nucleus.

As pointed out in ref 1, one should really be determining the value of s which minimizes $\bar{E}_s(R)$ for a fixed R , not a fixed sR . We do this by calculating $\bar{E}_s(R)$ from eq 2 for a particular R , starting from several different values of sR , and then fitting to a quadratic to get the minimum energy and best scaling factor. The expectation value of the quadrupole moment is obtained by quadratic interpolation of the values obtained from the scaled wave functions.

The energies and molecular quadrupole moments for CO calculated in this way from scaled N_2 wave functions are given in Table IA; the energies and molecular quadrupole moments for N_2 calculated from scaled CO wave functions are given in Table IB. We have also included, in Table II, comparison with the values obtained by direct calculation by Nesbet,³ whose expectation values we have used.

The similarities in physical and other properties between CO and N_2 have been frequently noted,^{4,5}

(4) For example, Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," translated and revised by M. A. Partridge and D. O. Jordan, Dover Publications, Inc., New York, N. Y., 1964, p 136; J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 134; J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 684.

and sometimes ascribed to similarities in electronic structure. Long and Walsh⁵ have argued that most of these properties follow from similar molecular size and external force field (which is expected from the relative positions of the C, O, and N atoms in the periodic table), while properties which reflect electronic structure, such as the effect of ionization on the bond strength, actually point up dissimilarities between the molecules.

The present results tend to bear out this idea. Similar electronic wave functions would imply very good results for the electronic properties of CO from scaled N₂ wave functions and *vice versa*. We note that the scaling factors are quite close to unity (compare ref 1), again reflecting similar molecular size, but that the agreement in energy is not very good. The energy errors are of the same order of magnitude as in the LiF-BeO pair,¹ which would certainly not be considered similar. Equilibrium internuclear distances are well predicted, but this again reflects only similar molecular sizes; the agreement for the molecular quadrupole is not very good.

The difference between the Hamiltonian for CO and N₂ is a one-electron operator, and perturbation theory has been employed to calculate its effect.⁶ Perturbation methods, because of their flexibility, can do much better than the present method, but it turns out that even energies as accurate as these reported here require considerable labor.

(5) L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, **43**, 342 (1947).

(6) T. Y. Chang and W. B. Brown, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-114 (1965).

The Electron Spin Resonance Absorption of Solid 1,1-Diphenyl-2-picrylhydrazyl Mixtures. Surface and Aging Effects

by Kedma H. Bar-Eli and Karl Weiss

Tyco Laboratories, Inc., Waltham, Massachusetts 02154, and Photochemistry and Spectroscopy Laboratory, Northeastern University, Boston, Massachusetts 02115 (Received October 29, 1965)

Matsunaga and McDowell¹ have reported that the electron spin resonance spectra of mixtures of 1,1-diphenyl-2-picrylhydrazyl (DPPH) with zinc oxide and with nickel oxide show line broadening and an apparent loss of spins when compared with the spectra of DPPH itself. This effect has been ascribed to a

transfer of electrons between DPPH and the oxides. DPPH admixed with inert solids is widely employed as a standard in electron spin resonance spectroscopy.² In this note we show that an interaction leading to loss of spins can occur even with materials considered to be inert. The extent of spin loss depends on the nature of the material and on the method of mixing.

The measurements were made with a standard Varian V-4500 spectrometer using a single cavity. DPPH (Aldrich Chemical Co.) was used either as received or after recrystallization,^{2b} with identical results. Calcium carbonate (Mallinckrodt Analytical reagent), magnesium carbonate, basic (Fisher Certified), and potassium chloride (Baker Analyzed) were used without further treatment. The mixtures were examined in air as weighed samples of constant volume.

A Wig-L-Bug amalgamator (Crescent Dental Manufacturing Co.) served to prepare mixtures of varying DPPH content. For *unground* mixtures the components were merely shaken until homogeneous. For *ground* mixtures (1-min grinding time), a stainless steel ball was included. Once homogeneity was attained by either method, the esr signal amplitude was independent of further mixing. The average particle diameter of DPPH and mixtures with KCl is $>50\ \mu$ before grinding and $\sim 5\ \mu$ after grinding measured by a Fisher Sub-Sieve Sizer. The particle size of MgCO₃ mixtures was determined by the carbonate itself which is $<0.5\ \mu$. Intensities were computed from the amplitude of the derivative curve and the line width, which was found to be invariant within each set of samples.³

The results are summarized in Figures 1 and 2 as plots of the specific intensity (I_{sp} , intensity per milligram of DPPH) against the weight fraction of DPPH in the mixture (X_D). The behavior of unground samples is illustrated by magnesium carbonate mixtures, which show the anticipated lack of dependence of I_{sp} on X_D . Fresh, ground mixtures with potassium chloride (Figure 1) also behave as expected. With ground magnesium carbonate and calcium carbonate mixtures, however, there is a marked decrease of I_{sp} with increasing dilution. That a rapid destruction of spins occurs during the grinding process is supported by a corresponding decrease in the apparent extinction coefficient of DPPH at 525 m μ observed in chloroform extracts of the ground magnesium carbonate mixtures.

(1) Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, **38**, 724 (1960).

(2) (a) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworth and Co. Ltd., London, 1958, Chapter 3; (b) J. J. Lothe and G. Eia, *Acta Chem. Scand.*, **12**, 1535 (1958); (c) L. S. Singer, *J. Appl. Phys.*, **30**, 1463 (1959); (d) J. Zanchetta, A. Marchand, and A. Pacault, *Compt. Rend.*, **258**, 1496 (1964).

(3) *Cf.*, however, F. Bruin and M. Bruin, *Physica*, **22**, 129 (1956).