

<sup>7</sup> R. W. Fessenden and R. H. Schuler, "ESR Spectra of Fluorinated Ethyl Radicals" (to be published). Presented (in part) at the 151st American Chemical Society Meeting, Pittsburgh, Pa., March 1966.

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<sup>8</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **43**, 2704 (1965).

<sup>9</sup> W. M. Tallis and W. D. Gwinn, *J. Chem. Phys.* **36**, 1119 (1962). In SF<sub>4</sub>, two fluorines are located approximately axially with the other two and the lone electron pair each occupying a (trigonal) equatorial position.

## Error Bounds for Expectation Values\*†

PHILIP JENNINGS AND E. BRIGHT WILSON, JR.

*Mallinckrodt Chemical Laboratories, Harvard University  
Cambridge, Massachusetts*

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EXPECTATION values  $\langle \phi B \phi \rangle$  for an unbounded operator  $B$  calculated from an approximate wavefunction  $\phi$  obviously have little value without some estimate of the limits of error. Bazley and Fox<sup>1,2</sup> used Schwarz's inequality to obtain the bounds

$$\begin{aligned} \Delta &= | \langle \psi | B | \psi \rangle - \langle \phi | B | \phi \rangle | \\ &= | \langle \psi | B | \psi \rangle - \langle \psi | B | \phi \rangle + \langle \psi | B | \phi \rangle - \langle \phi | B | \phi \rangle | \\ &= | \langle \psi | B | (\psi - \phi) \rangle + \langle (\psi - \phi) | B | \phi \rangle | \\ &\leq \epsilon (\langle \psi | B^2 | \psi \rangle^{\frac{1}{2}} + \langle \phi | B^2 | \phi \rangle^{\frac{1}{2}}), \quad (1) \end{aligned}$$

where

$$\epsilon^2 = \langle (\psi - \phi) | (\psi - \phi) \rangle \leq (\langle \phi | H | \phi \rangle - E_0) / (E_1 - E_0)$$

is Eckart's relation<sup>3</sup> involving the true Hamiltonian  $H$  and the correct energies  $E_0$  and  $E_1$  of the two lowest states (of given symmetry). Since experimental data are often available for energies, an upper bound to  $\epsilon$  can frequently be calculated.

When a very good wavefunction is available, but a simpler trial function is used to calculate expectation values as a matter of computational convenience, then  $\epsilon$  may be estimated from the overlap with the good wavefunction; i.e.,  $\epsilon = [2(1 - \langle \phi | \psi \rangle)]^{\frac{1}{2}}$ . This could give a

much better value than does the Eckart condition, which can be quite inefficient.

With very good functions  $\phi$ , a satisfactory approximation to replace  $\langle \psi | B^2 | \psi \rangle^{\frac{1}{2}}$  in Eq. (1) is obviously  $\langle \phi | B^2 | \phi \rangle^{\frac{1}{2}}$ . However, it is desirable to have a test for the adequacy of this approximation and one can be obtained by applying Eq. (1) again by replacing  $B$  everywhere by  $B^2$ . If then  $\langle \psi | B^4 | \psi \rangle$  is replaced by  $\langle \phi | B^4 | \phi \rangle$  and the whole expression expanded in powers of  $\epsilon$ , the result is, to order  $\epsilon^2$ ,

$$\Delta \lesssim 2\epsilon \langle \phi | B^2 | \phi \rangle^{\frac{1}{2}} + \epsilon^2 \langle \phi | B^4 | \phi \rangle^{\frac{1}{2}} / \langle \phi | B^2 | \phi \rangle^{\frac{1}{2}}. \quad (2)$$

Although this expression is not claimed to be a mathematically rigorous<sup>4</sup> set of bounds, it seems clear that when  $\epsilon$  is sufficiently small and  $\langle \phi | B^4 | \phi \rangle^{\frac{1}{2}} / \langle \phi | B^2 | \phi \rangle^{\frac{1}{2}}$  is near unity, it should be practically useful.

By repetition of the use of Eq. (1), the series in  $\epsilon$  can be extended, but, at least in the cases so far tested, interestingly close bounds are obtained only for rather small  $\epsilon$ , for which cases the term in  $\epsilon^2$  has not been very important.

If  $B$  is replaced by  $B$  plus a constant,  $\Delta$  is unchanged but  $\langle \phi | B^2 | \phi \rangle$  is altered and can be minimized by a proper choice. To first order in  $\epsilon$ , this gives

$$\Delta_1 \leq 2\epsilon (\langle \phi | B^2 | \phi \rangle - \langle \phi | B | \phi \rangle^2)^{\frac{1}{2}}. \quad (3)$$

Table I shows the numerical application of Eq. (3) to the ground state of helium, with several approximate variation functions. The fifth column is the contribution of the terms in  $\epsilon^2$ . The error limits calculated are seen to be considerably too large, except perhaps for the very best variation functions. Note, however, that the value of  $\langle r_{12} \rangle$  calculated by Knight and Scherr lies outside the error bounds for Pekeris' value.

It should be noted that special forms for  $\phi$  may permit much narrower bounds to be determined than those given by this method.<sup>5</sup> Thus, it has been argued that Hartree-Fock wavefunctions give much better expectation values for one-electron operators than would be indicated by Eqs. (1) or (2).

It is obvious that Eq. (3) provides a variational principle for expectation values since  $\phi$  can be varied to minimize the error bounds. However, with the oper-

TABLE I. Expectation-value bounds for He (atomic units).

Wavefunction	$\epsilon$	$\langle r_{12} \rangle$	$\Delta_1$	$\Delta_2$	$\langle (r_1 + r_2) / r_{12} \rangle$	$\Delta_1$	$\langle r_1 r_2 \cos \theta_{12} \rangle$	$\Delta_1$
Unscreened	0.448	1.094	0.50	0.22	1.563	0.85	0.0	0.24
Screened <sup>a</sup>	0.266	1.296	0.35	0.08	1.563	0.49	0.0	0.20
Two-term Hylleraas <sup>a</sup>	0.128	1.373	0.18	0.02	1.451	0.19	-0.0875	0.11
Three-term Hylleraas <sup>a</sup>	0.042	1.410	0.064	0.002	1.4485	0.06	-0.0629	0.035
Knight and Scherr <sup>b</sup>	$2.5 \times 10^{-4}$	1.4217	$4 \times 10^{-4}$	$7 \times 10^{-8}$	1.4489	$4 \times 10^{-4}$	-0.06475	$2 \times 10^{-4}$
Pekeris <sup>c</sup>	$5.5 \times 10^{-5}$	1.4221	$1 \times 10^{-4}$	$4 \times 10^{-8}$	...	...	-0.06474	$5 \times 10^{-5}$

\* Taken from L. C. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., Inc., New York, 1934), p. 224. These are, respectively, Functions 2, 7, 8 of that reference.

<sup>b</sup> R. E. Knight and C. W. Scherr, *J. Chem. Phys.* **40**, 3034 (1964) (sixth-order

perturbation-theory result). Actually, Knight and Scherr's 13th-order energy is not exactly the same as  $\langle \phi H \phi \rangle$  for their sixth-order  $\phi$ , but the difference should not be great.

<sup>c</sup> C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959) (1078-term function).

ators in the table, the error bounds thus determined do not seem to differ much from those obtained with the  $\phi$  given by energy minimization.

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<sup>1</sup> N. W. Bazley and D. W. Fox, *Rev. Mod. Phys.* **35**, 712 (1963).

<sup>2</sup> N. W. Bazley and D. W. Fox, *J. Math. Phys.* **7**, 413 (1966).

<sup>3</sup> C. Eckart, *Phys. Rev.* **36**, 878 (1930).

<sup>4</sup> In some cases Eq. (2) obviously diverges. Thus, for an  $s$  electron and  $B=1/r^2$ , the whole approach of Eq. (1) fails because  $\langle B^2 \rangle$  diverges. For  $B=1/r$ , Eq. (1) is all right but the  $\epsilon^2$  term in Eq. (2) diverges. It is likely, however, that the terms before divergence occurs are still useful as practical bounds if  $\phi$  is a sufficiently good approximation.

<sup>5</sup> W. A. Klemperer and J. Goodisman, *J. Chem. Phys.* **38**, 721 (1963).

## Notes

### Solubility and Thermodynamics of Solution of Argon in Mixtures of H<sub>2</sub>O and D<sub>2</sub>O

A. BEN-NAIM\*

*Department of Physical Chemistry, Hebrew University  
Jerusalem, Israel*

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IN this note we report measurements of the solubility (Table I) of argon in three mixtures of D<sub>2</sub>O and H<sub>2</sub>O. The question posed for this work was the following: The thermodynamic functions associated with the dissolution of inert gases in water give a rough indication of the structural state of the solvent.<sup>1-3</sup> There is some evidence<sup>4</sup> that liquid D<sub>2</sub>O has a higher "degree of crystallinity" which means that the average cluster size is larger in D<sub>2</sub>O than in H<sub>2</sub>O. On the other hand some theoretical considerations, based on a very simplified model<sup>1,2</sup> indicate that the thermodynamic functions of solution of gases in water are strongly dependent on the average cluster size. The question now arises, does the addition of increasing amounts of D<sub>2</sub>O to water increase or decrease the degree of crystallinity of the solvent. We know that addition of different solutes to water causes different effects on the struc-

TABLE I. Ostwald coefficient ( $\gamma \cdot 10^3$ ) for argon in mixtures of H<sub>2</sub>O and D<sub>2</sub>O ( $X$  is mole fraction of D<sub>2</sub>O).

$t^\circ\text{C}$	5	10	15	20	25
$x=0.03$	48.60	43.70	39.81	36.85	34.15
$x=0.5$	51.15	45.66	41.27	38.18	35.28
$x=0.9$	53.56	47.66	43.18	39.38	36.46

TABLE II. Thermodynamic functions for the transfer of argon from H<sub>2</sub>O into mixtures of H<sub>2</sub>O and D<sub>2</sub>O at 20°C ( $X$  is mole fraction of D<sub>2</sub>O).

	$X=0.03$	$X=0.5$	$X=0.9$	$X=1$
$\Delta\mu_t^\circ$ (cal/mole)	-3.5	-24.0	-42.0	-49.8
$\Delta\bar{S}_t^\circ$ (eu)	-0.25	-0.5	-0.8	-0.77
$\Delta\bar{H}_t^\circ$ (cal/mole)	-77	-170	-276	-275

tural state of water,<sup>5</sup> some nonionic solutes, at very low concentration, may increase the degree of crystallinity, while others decrease it. D<sub>2</sub>O, considered as a solute in H<sub>2</sub>O, has a peculiar place in this respect: It is not an inert solute so we do not expect a "stabilizing effect" of the kind revealed by some nonelectrolytes.<sup>1,2</sup> Hence there remain two possibilities: one of which is that the D<sub>2</sub>O molecule fits in the framework of the clusters of H<sub>2</sub>O molecules. (Note that for the present argument it is not essential to know the amount of HDO formed. The determining factor is the O-O distance in the cluster and not the relative proximity of H or D to a particular oxygen atom.) In this case owing to the higher energy of the hydrogen bond O...D-O we might expect that the average cluster size will increase. On the other hand if it does not fit into the framework of the cluster, it should cause a breakdown of the cluster size since its presence dilutes the H<sub>2</sub>O molecules and hence reduces the probability of their coming together to form a cluster. In the latter case we would expect that both the entropy and the enthalpy of transfer of argon from pure H<sub>2</sub>O into mixtures of H<sub>2</sub>O/D<sub>2</sub>O will be positive for the same reasons as in the case of the effect of a solute which causes a destabilizing effect.<sup>5</sup>

The thermodynamic functions<sup>6</sup>  $\Delta\mu_t^\circ$ ,  $\Delta\bar{S}_t^\circ$ , and  $\Delta\bar{H}_t^\circ$  which were calculated for the transfer of argon from pure water into mixtures of D<sub>2</sub>O and H<sub>2</sub>O show a monotonic (nearly linear) change when changing the solvent from pure water to pure D<sub>2</sub>O (Table II and Fig. 1). This might indicate that the O...D bonds not only fit into the framework of the clusters of O...H bonds, but also increase gradually the average cluster

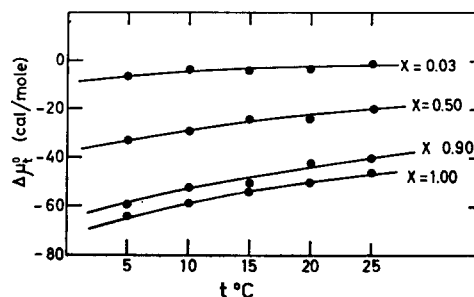


FIG. 1.  $\Delta\mu_t^\circ$  for the transfer of argon from H<sub>2</sub>O to mixtures of H<sub>2</sub>O and D<sub>2</sub>O at different mole fraction  $X$  of D<sub>2</sub>O.