

We next solve the eigenvalue problem $H^l\psi = E\psi$. Using the definition of $H^{l,0}$, we obtain an integral equation for ψ ,

$$(E_{l+1}^0 - E + H')\psi = \sum_{i=1}^l (E_{l+1}^0 - E_i^0) \langle \psi_i^0 | \psi \rangle \psi_i^0. \quad (1)$$

If H' is a multiplicative operator, then ψ must be a linear combination of the functions $\psi_i^0 / (E_{l+1}^0 - E + H')$, $i = 1, \dots, l$. Substituting this form for ψ into (1) yields the secular equation

$$\det | \delta_{ij} (E_{l+1}^0 - E_i^0)^{-1} - \langle \psi_i^0 | (E_{l+1}^0 - E + H')^{-1} | \psi_j^0 \rangle | = 0. \quad (2)$$

The l lowest roots of (2) are the desired lower bounds to the l lowest eigenvalues of H .

Equation (2) can formally be generalized to include the cases where H' is not necessarily multiplicative by considering $(E_{l+1}^0 - E + H')^{-1}$ to be the inverse operator of $(E_{l+1}^0 - E + H')$. In one of their procedures,³ Bazley and Fox replace H' by its inner projection onto a finite subspace, whereby the problem of inverting $(E_{l+1}^0 - E + H')$ is reduced to the inversion of a finite matrix. This method has the advantage that integrals of the multiplicative operator $(E_{l+1}^0 - E + H')^{-1}$ are avoided, but the limitation that H' must be a positive operator. Also the intermediate Hamiltonian itself becomes intrinsically less efficient with the projection of H' . We note that the secular equation obtained by Bazley and Fox³ does reduce to Eq. (2) of this paper if in their derivation the first projection of H' is omitted and the optimum value of the constant γ is incorporated into their secular equation.

As a test of the usefulness of our method, we have applied it to a standard example—the S states of the helium atom. The results appear in Table I and are compared to upper bounds given by Pekeris.⁴ The integrals required were computed by using a Gauss-Laguerre quadrature of order 25.⁵

TABLE I. Bounds for the eigenvalues of helium (atomic units).

State	Unperturbed energy	Upper bound ^a	Lower bound ^b	Difference
1s ³	-4.0000	-2.9037	-2.9762	0.0725
1s2s	-2.5000	-2.1460	-2.1596	0.0136
1s3s	-2.2222	-2.0613	-2.0658	0.0045
1s4s	-2.1250	-2.0336	-2.0356	0.0020
1s5s	-2.0800	-2.0212	-2.0218	0.0006
1s6s	-2.0556	-2.0146	-2.0154	0.0008
1s7s	-2.0408	-2.0106	-2.0110	0.0004
1s2s	-2.5000	-2.1752	-2.1802	0.0050
1s3s	-2.2222	-2.0687	-2.0704	0.0017
1s4s	-2.1250	-2.0365	-2.0373	0.0008
1s5s	-2.0800	-2.0226	-2.0227	0.0001
1s6s	-2.0556	-2.0154	-2.0157	0.0003
1s7s	-2.0408	-2.0111	-2.0114	0.0003

^a See Ref. 3.

^b This was done using a truncation of H^0 of order $l=9$.

There are several points to note in summary. First, it is encouraging that we do not need matrix elements of H^2 as are required in the older methods of Temple⁶ and Weinstein.⁷ The difficulty involved in computing $\langle H^2 \rangle$ seems to be one of the major reasons that few lower bounds have been calculated.

Second, there is no restriction that H' be positive as is required in the methods based on performing an Aronszajn projection of $H^{l,0}$.³ In the calculations reported in Table I, we used a bare nucleus H^0 with $H' = r_{12}^{-1}$, but there is no reason why one could not use a screened H^0 with H' appropriately modified (this H' will not be positive). We would certainly expect this to give better results than ours presented here.

Third, we notice that the lower bounds are better the higher the state. This behavior is expected, however, for $H^{l,0}$ has the same l lowest eigenvalues as H^0 ; and, since E_i^0 itself is a better lower bound to E_i as i increases, we expect that the i th eigenvalue of $(H^{l,0} + H')$ will be a better lower bound to the i th eigenvalue of $(H^0 + H')$ as i increases.

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¹ N. W. Bazley and D. W. Fox, Phys. Rev. **120**, 144 (1961); **124**, 483 (1961). Other references are given in these papers.

² $A < B$ means $\langle \phi A \phi \rangle < \langle \phi B \phi \rangle$ for arbitrary ϕ in the domains of A and B .

³ N. W. Bazley and D. W. Fox, J. Math. Phys. **3**, 469 (1962).

⁴ C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

⁵ A. H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, to be published).

⁶ G. Temple, Proc. Roy. Soc. (London) **A119**, 276 (1928).

⁷ D. H. Weinstein, Proc. Natl. Acad. Sci. (U.S.) **20**, 529 (1934).

Empirical Correlations among Monohydride Bond Lengths

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A log-log plot of X-H equilibrium internuclear distance vs atomic number exhibits a remarkable linearity for the monohydrides of first- and second-row elements (see Fig. 1). Also plotted for comparison are all other spectroscopically known monohydrides.¹ Although the heavier monohydrides fall into a regular pattern according to period, there is considerable scatter from any linear relationship. Least-squares assignment of the best linear fit yields the following empirical relations: Row I (LiH to HF), $R_e = 2.72 Z^{-0.496}$; Row II (NaH to HCl), $R_e = 16.09 Z^{0.893}$.

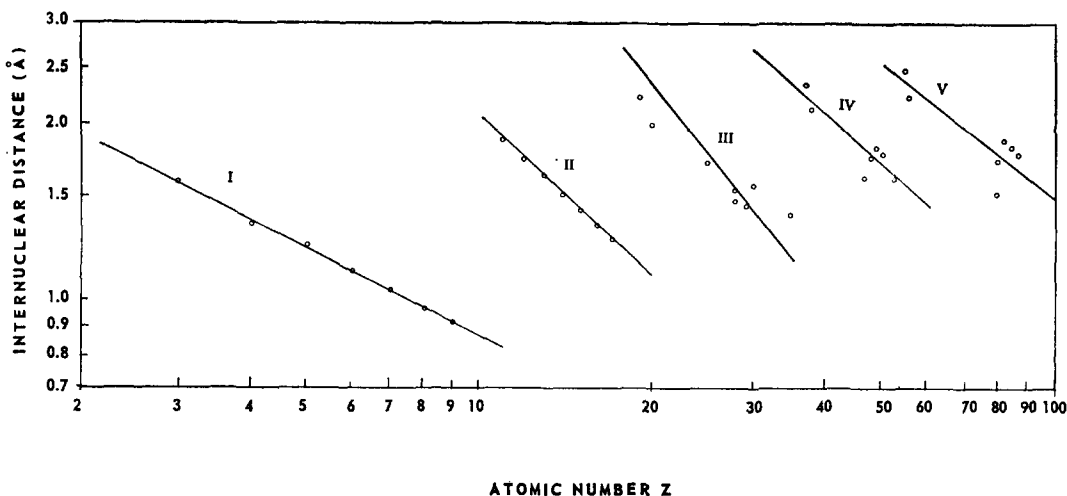


FIG. 1. Log-log plot of equilibrium internuclear distance vs atomic number for monohydrides, Rows I-V.

No relation between empirical atomic radius² and atomic number shows as regular a variation as that found above for the first- and second-row elements; neither do analogous plots of monochloride or monoxide bond lengths. It is interesting, however, to note that log-log plots of empirical atomic radius vs Z have almost exactly twice the slope of R_e vs Z , suggesting a geometric-mean relationship

$$R(X-H) \approx [(2R_H)(2R_X)]^{\frac{1}{2}}$$

for elements of the first two rows.

¹ All data are taken from G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company Inc., Princeton, New Jersey, 1950), Appendix.

² See, for example, J. C. Slater, *Quart. Progr. Rept.* **54**, 4 (1964).

On the Electrical Conductivities of Tetracyanoquinodimethan Anion-Radical Salts*

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SALTS of the anion radical of 7,7,8,8-tetracyanoquinodimethan (TCNQ)¹⁻³ exhibit electrical conductivities whose magnitudes depend strongly on the nature of the cation.²⁻⁶ For example, salts with metal cations generally have low to intermediate conductivities, whereas, as Acker and Blomstrom³ note, a sufficient condition for high conductivity is that the cation be a planar, aromatic heterocyclic molecule. Indeed, several TCNQ salts with aromatic cations show metallic behavior: temperature-independent conductivities as high as $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ and temperature-independent paramagnetic susceptibilities.⁴⁻⁶

Though variations in steric factors surely play a role, we propose that the electronic polarizability of the cation is a more important determinant of the varia-

tion in conductivities. The mechanism through which this can occur was suggested by Little⁷ in another connection. Its operation in the TCNQ salts is best visualized beginning with a Heitler-London model for conductivity and applying Mott's criterion for the metal-semiconductor transition.⁸

From known crystal structures^{9,10} and conductivity anisotropies^{3,5,11} of these salts it is clear that conductivity arises from motion of the odd π electrons among the TCNQ sites. The TCNQ molecules are arranged in face-to-face stacks such that the π -orbital overlap between molecules within a stack is considerably larger than that between near neighbors in an aromatic hydrocarbon crystal. Guided by previous studies of band structures in aromatic hydrocarbon crystals,^{12,13} we estimate a width Δ of the order of 0.1 eV for the tight binding energy band based on the lowest unoccupied π orbitals of the TCNQ molecules.

As this estimate of Δ is small compared with the expected Coulomb repulsion energy of the odd electrons, one expects the band model to give a poor description of crystal states. Indeed, the majority of the known TCNQ salts are semiconductors though formally they have partly filled bands.²⁻⁶ In a Heitler-London model this difficulty does not exist. The odd electrons are considered in first approximation to be localized and, in the ground state, to occupy highly ordered positions so as to minimize their mutual Coulomb repulsions: e.g., one and only one electron on each TCNQ site in the simple salt $M^+TCNQ^{\cdot-}$, one electron on every alternate TCNQ site in the complex salt $M^+TCNQ^{\cdot-}TCNQ^0$, etc. These are nonconducting states.

Conducting states arise from introduction of defects into the ordered ground-state configuration. For the simple salt an odd electron is removed from one $TCNQ^{\cdot-}$, leaving a $TCNQ^0$, and added to a distant