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Dependence of Induction and Dispersion Energies at Finite Internuclear Distances*†

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The usual calculations of induction and dispersion energies lead to divergent series in negative powers of the distance R which have been interpreted as asymptotic expansions. The system composed of a normal hydrogen and a proton at a finite separation is treated by an extended variation method, leading to Euler equations for the perturbed wave functions. Solutions in terms of known functions are used to calculate the two principal terms of the second-order energy for a number of values of R. The method is found to lead to convergent results for all values of R, and to be compatible with the virial theorem. Extension to more complex cases and to dispersion is qualitative. A variation calculation, using traditional and other plausible trial functions with the correct potential, is compared.

The series in negative powers of R are found to be neither quantitatively nor qualitatively good representations of induction effects at chemically interesting distances. Similar behavior is inferred for dispersion.

I. INTRODUCTION

INDUCTION and dispersion energies for a system of two atoms separated by a distance R are calculated by second-order perturbation or equivalent variation methods. The traditional procedures[1,2] include assumptions mutually consistent only for infinite separation. The series thus obtained are divergent for all finite distances.[3] Such developments, representing a function in the sense of Poincaré, may be useful for obtaining numerical values when the coefficients are accurately known.[3,4]

We are aware of three fundamental limitations to the general use of such series in inverse powers of R for induction and dispersion effects:

1. Accurate values of a number of coefficients must be available in order to know when to stop. Furthermore, for small and moderate values of the variable, the series may be useless, the second term being already as large as the first.
2. An important class of functions possesses no asymptotic expansion, or more precisely, possesses a common expansion with all coefficients identically zero. Terms of importance for finite arguments, but disappearing more rapidly than any finite power at infinity, such as the exponential, are in this class.[5] For the incomplete gamma function which will enter our calculations, there is a one-term approximation asymptotic to the function, but the error must be determined by comparing this approximation with the function.
3. Even when a given function is shown to be represented by a particular asymptotic expansion, it does not follow that its derivative is similarly represented by the derivative of the same expansion.[6] The derivatives of a molecular potential are frequently of greater interest than its numerical values at selected points.

The unrestricted variation method outlined below may be considered an extension of methods developed by Slater and Kirkwood,[7] by Coulson,[1] and by Pople and Schofield.[8] To expose particular facets of this problem, it will be convenient to consider selected relevant polarizability calculations; a more complete survey and critique may be found in Allen's[9] recent paper. We shall be interested in distances of one to ten atomic units (0.52917×10^{-8} cm) and interaction energies less than one unit (27.2097 ev), and shall use these units exclusively. Relativistic effects (retardation, etc.) will not be significant.

II. UNRESTRICTED VARIATION METHOD. POLARIZABILITY OF THE NORMAL HYDROGEN ATOM

In the presence of the potential V, the wave function for the unperturbed system Ψ_0 becomes

$$\Psi=\sum_n \Psi_n, \tag{1}$$

where the Ψ_n shall be made mutually orthogonal and may be taken as real throughout this paper. Similarly with the Hamiltonian and energies:

$$H=H_0+V, \tag{2}$$

$$E=E_0+E_1+E_2+\cdots E_n+\cdots, \tag{3}$$

and, taking the potential as of first order, the wave functions and energies of nth orders, respectively, we

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separate orders:

$$E_0\langle 0|0\rangle=\langle 0|0|0\rangle, \tag{4a}$$

$$E_1\langle 0|0\rangle=\langle 0|1|0\rangle, \tag{4b}$$

$$E_2\langle 0|0\rangle=\langle 1|0-E_0|1\rangle+2\langle 0|1|1\rangle, \tag{4c}$$

$$E_3\langle 0|0\rangle=\langle 1|1-E_1|1\rangle, \tag{4d}$$

$$E_4\langle 0|0\rangle=\langle 2|0-E_0|2\rangle+2\langle 1|1|2\rangle-E_2\langle 1|1\rangle. \tag{4e}$$

Ψ_1 may be varied to minimize E_2 if (4a) is satisfied:

$$(H_0-E_0)\Psi_1=-V\Psi_0, \tag{5}$$

from which automatically

$$E_2\langle 0|0\rangle=\langle 0|1|1\rangle. \tag{6}$$

The formal substitution

$$\Psi_1=u\Psi_0, \tag{7}$$

followed by transformation of the kinetic operator, eliminates a term $[(H_0-E_0)\Psi_0]u$, leading to the equation at the base of the formalism of Pople and Schofield. For the one-electron case, it is

$$\nabla(\Psi_0{}^2\nabla u)=2V\Psi_0{}^2. \tag{8}$$

We have examined the validity of the polyelectronic equivalent and find it to be the correct first-order equation as long as (4a) is satisfied.[10]

Calculating the uniform field polarizability of the normal hydrogen atom corresponds to using the potential

$$V=-Fr\cos\theta. \tag{9}$$

Equation (8) separates on the substitution

$$U=Fg(r)\cos\theta, \tag{10}$$

leading to the solution

$$g(r)=(r+r^2/2). \tag{11}$$

This so far is entirely equivalent to the calculation of Slater and Kirkwood,[7] which in turn agrees with the solution of the wave equation for an atom in the field by Epstein[11]; the polarizability obtained is 4.5. A close variation method approximation is the trial function

$$g(r)=are^{br}, \tag{12}$$

yielding $b=0.195$; $\alpha=4.476$.

The Raleigh-Schrödinger perturbation theory was applied to this problem by Tillieu and Guy[12] who calculated eleven terms. Estimating the rest of the discrete spectrum gives only 3.66. The continuum is therefore not negligible. However, expansion in the discrete complete set of Laguerre radial functions, first utilized by Schrödinger and recently revived by Löwdin,[13] for which we propose the name Schrödinger-Löwdin functions, leads to the exact result in only two terms. The simple Hassé-Kirkwood form

$$u=\lambda V,\quad \lambda=\text{constant}, \tag{13}$$

leads to only 4.0.

III. THE HYDROGEN MOLECULE-ION AS A PERTURBED ATOM

The perturbation of a normal hydrogen atom by a proton at distance R corresponds to a potential

$$V=1/R-1/|\mathbf{R}-\mathbf{r}|, \tag{14}$$

which may be expanded in two series:

$$V=-\sum_{n=1}^{\infty} r^n/R^{n+1}P_n(\cos\theta),\quad \text{Region I: } r\leqslant R \tag{15a}$$

$$=1/R-\sum_{n=0}^{\infty} R^n/r^{n+1}P_n(\cos\theta),\quad \text{Region II: } r\geqslant R. \tag{15b}$$

This piecewise expansion is absolutely convergent almost everywhere. Substitution of (15a) in Eq. (8) with

$$u=g_n(r)P_n(\cos\theta) \tag{16}$$

leads to

$$g_n(r)=[r^n/n+r^{n+1}/(n+1)]1/R^{n+1}, \tag{17}$$

while

$$E_2=-\tfrac{1}{2}\sum_{n=1}^{\infty}\alpha_n/R^{2n+2}, \tag{18}$$

and

$$\alpha_n=(2n+1)!(n+2)/n\times 2^{2n}; \tag{19}$$

therefore

$$E_2=-\sum_{n=1}^{\infty} 2\frac{(2n+1)!(n+2)}{n\times(2R)^{2n+2}}. \tag{20}$$

However, the integration over r has been carried over the interval 0 to ∞ in calculating α_n, despite the restriction on (15a). Brooks[3] noted the divergence of a series corresponding to (20), although his method leads to an incorrect expression for α_n. Working with Unsöld's approximation to the second-order energy, he attempted to remedy this defect in arresting the integration at $r=R$. This produces a convergent series in incomplete gamma functions. Roe[14] showed that this series no longer corresponded to the Unsöld formula by obtaining both the sum of Brooks' series and the Unsöld expression in terms of known functions.

A similar series could be obtained here by interrupting the integration. However, this would be inconsistent with the method, for the transformation of the kinetic operator presumed continuous wave functions with continuous first derivatives. A discontinuous wave function contributes infinitely to the kinetic energy, while a discontinuity of the derivative leads only to a

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finite contribution. There is, however, no particular need to neglect the negative multipoles, or series (15b).

The first consequence of using both series of (15) is that the first-order energy no longer vanishes:

$$E_1=(1+1/R)e^{-2R}. \tag{21}$$

Next, a solution to Eq. (8) is readily obtained for region II, such that

$$g_{\mathrm{II}}(r)=-R^n\left[\frac{1}{(n+1)r^{n+1}}+\frac{1}{nr^n}\right]. \tag{22}$$

But the composite function, $g_{\mathrm{I}}(r)$, is not yet continuous,

$$g_{\mathrm{I}}(r)=\frac{1}{R^{n+1}}\left[\frac{r^n}{n}+\frac{r^{n+1}}{n+1}\right], \tag{17}$$

and is not even of the same sign as $g_{\mathrm{II}}(r)$ at $R=R$. These are solutions of an inhomogeneous second-order differential equation; the homogeneous equation obtained by suppressing the potential has two solutions, one regular in the first region, the other acceptable in the second, which may be used to make it and its first derivative continuous at $r=R$. The solution acceptable in the first region is

$$f_{\mathrm{I}}(r)=r^ne^{2r}\int_0^1 e^{-2rt}t^{n+1}(t-1)^{n-1}dt \tag{18}$$

$$=r^ne^{2r}\sum_{j=0}^{n-1}\binom{n-1}{j}(-1)^jG_{n+j+2}(2r). \tag{19}$$

$G_n(x)$ is an incomplete gamma function[15] such that

$$G_n(x)=\int_0^1 e^{-xt}t^{n-1}dt \tag{20}$$

$$=\sum_{s=0}^{\infty}\frac{(-x)^s}{(s+n)s!} \tag{21}$$

$$=(n-1)!e^{-x}\sum_{\nu=0}^{\infty}\frac{x^\nu}{(n+\nu)!}. \tag{22}$$

It is easily established that this is a case of the confluent hypergeometric function of the first kind with the following convenient properties:

$$G_n(x)\approx\frac{e^{-x}}{n},\qquad x\ll n \tag{23}$$

$$\rightarrow(n-1)!/x^n,\quad x\gg n \tag{24}$$

$$G_n(x+h)=\sum_{m=0}^{\infty}\frac{(-h)^m}{m!}G_{(n+m)}(x), \tag{25}$$

$$G_n(x)=\frac{(n-1)!}{x^n}\left[1-e^{-x}\sum_{j=0}^{n-1}\frac{x^j}{j!}\right], \tag{26}$$

$$\frac{d}{dx}G_n(ax)=-aG_{n+1}(ax), \tag{27a}$$

$$\int_0^x t^{m-1}G_n(at)dt=\frac{x^m}{m-n}[G_n(ax)-G_m(ax)],\ m\neq n. \tag{27b}$$

Brooks' series could be readily expressed in terms of these functions. From (26) it is evident that neglect of the terms of exponential dependence may render divergent an otherwise convergent series in these functions.

The second solution to the homogeneous equation is a finite series in negative powers of r:

$$f_{\mathrm{II}}(r)=\frac{n!}{(2n)!r^{n+1}}\sum_{j=0}^{n+1}\frac{(2n-j)!2^jr^j}{(n+1-j)!j!}. \tag{28}$$

The second-order energy appears as a fourfold series. The terms arising from (17) and (22) are found to be bounded by convergent series for all R, vanishing at $R=0$. The terms arising from (19) and (28) are messy; convergence of the over-all expression is inferred indirectly.

Pieced together, the radial factors for the dipole perburbation are

$$g_{\mathrm{I}}(d)=\frac{1}{R^2}[(r+r^2/2)-Cre^{+2r}G_3(2r)], \tag{29a}$$

$$g_{\mathrm{II}}(d)=R\left[1-S\left(\frac{1}{2r^2}+\frac{1}{r}+1\right)\right], \tag{29b}$$

with

$$C=3(R+1)^2e^{-2R}, \tag{30a}$$

and

$$S=1-6(R+1)[G_2(2R)-G_3(2R)]. \tag{30b}$$

The energy expression contains only functions already defined,

$$E_2(2)=-\tfrac{1}{3}\{4RG_5(2R)+2R^2G_6(2R)$$
$$-2RC[G_3-G_5(2R)]+2Re^{-2R}[R-S(1+R)]\}. \tag{31}$$

The corresponding quadrupole terms are:

$$g_{\mathrm{I}}(q)=\frac{1}{R^3}\left\{\left(\frac{r^2}{2}+\frac{r^3}{3}\right)-Dr^2e^{2r}[G_4(2r)-G_5(2r)]\right\}, \tag{32a}$$

$$g_{\mathrm{II}}(q)=R^2\left[\frac{1}{3r}+\frac{1}{9}-T\left(\frac{1}{3r^3}+\frac{1}{2r^2}+\frac{1}{3r}+\frac{1}{9}\right)\right], \tag{32b}$$

where

$$D=10(R+1)(1+R+\tfrac{1}{3}R^2)e^{-2R}, \tag{33a}$$

$$T=1-30(R+1)[G_3(2R)-2G_4(2R)+G_5(2R)]. \tag{33b}$$

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TABLE I. Dipole term (columns I to VI) and quadrupole term (columns VII to XI). (I) Dipole contribution to second-order energy predicted by limiting function, $\alpha_1/2R^4$. $[-E_2(d)^\infty]$. (II) Dipole contribution to second-order energy calculated by method of this paper; $-\Delta E_2(d)$. (III) Ratio, II/I. (IV) Dipole contribution to second-order energy predicted by two parameter variation function, using correct potential. (V) Dipole contribution to second-order energy predicted by Hassé-Kirkwood type linear variation function with correct potential. (VI) Ratio, IV/I. (VII) Quadrupole contribution to second-order energy predicted by limiting function, $\alpha_2/2R^6$: $[-E_2^\infty(q)]$. (VIII) Quadrupole contribution to second-order energy calculated by method of this paper; $-\Delta E_2(q)$. (IX) Ratio, VIII/VII. (X) Ratio of quadrupole to dipole energies, predicted by limiting functions, VII/I. (XI) Ratio of quadrupole to dipole energies, predicted by method of this paper, VIII/II. All of the energies are negative.

R (a.u.)	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
1.5	0.4444	0.07093	0.1596	···	···	···	0.6584	0.01259	0.01912	1.4815	0.1775
2.0	0.1406	0.04908	0.3490	0.04755	0.4730	0.3382	0.1172	0.008589	0.07329	0.8333	0.1750
3.0	0.02778	0.01974	0.7105	0.01924	0.01873	0.6926	0.01029	0.003429	0.3332	0.3708	0.1737
4.0	0.008789	0.007931	0.9023	0.007843	0.007272	0.8924	0.001831	0.001156	0.6312	0.2083	0.1457
5.0	0.003600	0.003502	0.9726	0.003492	0.003146	0.9700	0.0004800	0.0004231	0.8815	0.1333	0.1208
7.5	0.0007111	0.0007106	0.9993	···	···	···	0.0000453	0.00004175	0.9216	0.0637	0.05875

so finally:

$$E_{2q}=-\left[\tfrac{2}{5}RG_7(2R)+(4/5)R^2G_8(2R)\right]+\tfrac{2}{5}D\left[G_5(2R)-2G_4(2R)+G_6(2R)\right]-\left[\frac{4R^3}{15}e^{-2R}-\frac{4R^4\bar{E}i(-2R)}{9}\right]+\frac{RTe^{-2R}}{45}\left[2R^2+5R+4\right]. \quad (34)$$

Numerical values of these terms for several values of R are displayed in Table I. Also in the table are the values of the asymptotic forms:

$$E_2^\infty(d)=-9/4R^4=-\tfrac{1}{2}\alpha_1/R^4, \quad (35)$$

$$E_2^\infty(q)=-15/2R^6=-\tfrac{1}{2}\alpha_2/R^6. \quad (36)$$

Within the framework of the ordinary variation method there is a consistent procedure which also yields convergent results. A trial function corresponding to

$$g(r)=C_0+C_1r+C_2r^2+\cdots \quad (37)$$

may be used with the correct potential. Column IV of Table I corresponds to using C_1 and C_2 while column V uses C_1 alone—the usual linear approximation of Kirkwood. One or two additional parameters add very little, while greatly complicating the solution.

Brooks and Roe were concerned with using the second-order energy to explain the difference between the results of the simple LCAO calculation of the molecular energy of H_2^+ and the accurate solution of the wave equation for that system. We note that our calculation, to third order

$$\Delta E=E_1+\Delta E_2+\Delta E_3, \quad (37)$$

predicts a binding energy of 0.0594 a.u. (atomic units) at the equilibrium separation. This is close to the reference calculation cited by Brooks and by Roe, which predicts a D_e of only 0.0648 a.u. The known value is 0.1026 a.u. There would necessarily be some slight improvement if the higher order multipole terms of the second-order perturbation were included; from Table II we see that it is better to include the terms of third order which may be calculated with the perturbed functions available.

Using these same perturbed functions as trial functions in an ordinary variation calculation, we simultaneously varied a linear coefficient λ and rescaled, obtaining $\Delta E=-0.05946$, η (scale factor)$=1.1484$, $\lambda=1.4757$. With neither scaling nor variation of a coefficient, this leads to -0.04726. This suggests that retention of more terms and higher orders would lead to a one-center expansion for the hydrogen molecule ion, rather than to an energy common to both attractive and repulsive states.

IV. DISCUSSION ENERGY. QUALITATIVE FEATURES

The interaction of two atoms on the same electrostatic model introduces a perturbation operator, in standard notation:

$$V=1/R-1/r_{2a}-1/r_{1b}+1/r_{12}, \quad (38)$$

where only three of the four variables can be independent. Usually one eliminates r_{12}, since

$$r_{12}=|\mathbf{R}-\mathbf{r}_{1a}+\mathbf{r}_{2b}|, \quad (39)$$

so that

$$V=1/R+1/|\mathbf{R}-\mathbf{r}_{1a}+\mathbf{r}_{2b}|-1/r_{2a}-1/r_{1b}. \quad (40)$$

The last three terms are then expanded in terms of R, r_{1a}, and r_{2b}. The subscripts a and b may then be dropped; the expansion requires four series.[16]

The traditional procedure is to consider only the first term of the first series, valid if

$$r_1+r_2\leqslant R. \quad (41)$$

In this region, one calculates a coefficient d such that

$$\lim_{R\to\infty} E_2(d,d)=-d/R^6. \quad (42)$$

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TABLE II. Relative importance of terms at $R=2$ a.u. Energies of second and third order as well as binding energy with potential and wave functions truncated at (a) dipole term, (b) quadrupole term, (c) octapole term. Some integrals were evaluated by numerical methods with possible error at the third significant figure.

	ΔE_2	ΔE_3	ΔE	
(a)	-0.04908	-0.00400	-0.01760	$\Delta E = E_1 + \Delta E_2 + \Delta E_3$
(b)	-0.05766	-0.01452	-0.04471	
(c)	-0.06020	-0.02222	-0.05494	$E_1(R=2) = +0.02747$

Hirschfelder and Löwdin,[13] using the Schrödinger-Löwdin functions, obtained the precise value of d for two normal hydrogen atoms 6.499026. The linear approximation and simplified perturbation calculations both lead to 6.0. The equations determining the optimum perturbed functions are no longer separable, so the direct method used here in the simpler problem is no longer practical. It is interesting that the quadratic variation function, which gives the correct uniform field polarizability

$$g(r) = C_1 r + C_2 r^2, \tag{43}$$

is still a rather fair approximation, corresponding to a coefficient d of 6.4821428, obtained by Hirschfelder and Löwdin at an intermediate stage of their accurate calculation, confirmed less precisely by direct variation calculation.

Analogy with the induction calculation suggests that a complete solution would be only moderately more complex, in particular would require piecing together solutions which would differ if the radial variable appeared as a positive or negative power in the potential in a variation calculation. A much more practical approach seems to be the extension to finite separation of the elegant method of Hirschfelder and Löwdin.[13] We should expect a more marked deviation from inverse power dependence at the same distance than in the induction case, since the interval of convergence of the first series is more restrictive:

$$r_1 + r_2 \leqslant R, \tag{41}$$

rather than

$$r_1 \leqslant R. \tag{15a}$$

It further seems evident that an ordinary variation calculation using the correct potential must lead to a finite second-order energy at all separations. Such a calculation would lead to integrals more messy than difficult, such as

$$\int_0^R \int_0^{R-r_1} r_1{}^m e^{-2r_1} r_2{}^n e^{-2r_2} dr_2 dr_1, \tag{44}$$

which becomes

$$R^{n+1} \sum_{\nu=0}^{m} (-1)^\nu \frac{m!}{(m-\nu)!} R^{m-\nu} \times \sum_{j=0}^{\nu} \frac{R^j}{2^{\nu-j+1} j!} \left[G_{n+1}(2R) - \frac{e^{-2R}}{n+j+1} \right]. \tag{45}$$

[The equivalence of m and n can be shown using the recurrence relation: $xG_k(x) = (k-1)G_{k-1}(x) - e^{-x}$.] This calculation would furnish only a lower bound to the magnitude of the interaction, bearing the same relation to the full solution as curve B of Fig. 1 does to curve A.

V. CONCLUSIONS

The series in inverse powers of R usually used for induction energies do not appear to be either qualitatively nor quantitatively good representations of this effect at chemically interesting distances. A similar behavior is to be expected for dispersion energies. The essential divergence of such series is a direct consequence of the incompatibility of the assumptions used in obtaining them. Brooks recognized the divergence, but failed to obtain an acceptable remedy because of his neglect to the multipoles of negative order and because of the limitations of the Unsöld formula. Papers by Sternheimer and colleagues and by Burns[17] indicate an awareness that both series must be used to represent the perturbing potential for induction calculations. Burns compares a numerical solution of Sternheimer's equations with a variation of parameters approach.

In semiempirical calculations on the simple ionic model, the repulsive potential is usually inferred by difference or arbitrarily assigned a high inverse power. A consistent term would correspond to the first-order energy of the sample calculation. Such a term could be readily calculated from the wave functions presently available for many ions. To the extent that the model is applicable there, one should expect a very serious deviation from inverse power behavior at about the equilibrium separation. The nth order energy for a hydrogenic atom of charge z perturbed by charge at distance R is

$$E_n(z,R) z^{2-n} E_n(1,zR), \tag{46}$$

and it appears from Burns' work that a similar relation holds for large isoelectronic systems. Thus the second-order dipole term, or even the whole second- and third-order energies might be approximated by incomplete gamma functions and exponentials as suggested by Brooks and on intuitive grounds by Frost and Woodson.[18]

A major difficulty of electrostatic models is their reconciliation with the virial theorem. For a molecular system in the Born-Oppenheimer approximation, it takes the form[19]

$$R dW_e/dR + 2W_e = \bar{V}_e, \tag{47a}$$

or

$$R dW_e/dR + 2\bar{T}_e + \bar{V}_e = 0, \tag{47b}$$

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where W_e is the molecular energy in the approximation. At the equilibrium distance it takes the well-known form

$$2\bar{T}_e+\bar{V}_e=0. \tag{48}$$

It is also known that the variation of a scale factor in a molecular energy calculation is sufficient to satisfy (48). Unfortunately, (47) will in general only be satisfied when it reduces to (48). In the calculation of Sec. III, the well-known first-order energy is entirely potential; (47) will probably not be satisfied for any finite R. At the second order, Ψ_1 was varied to minimize E_2 in

$$E_2=\langle 1|0-E_0|1\rangle+2\langle 0|1|1\rangle. \tag{4c}$$

Since the two terms of the right-hand side represent corrections to the kinetic and potential energies, respectively, varying even a linear parameter assures that (48) will hold for the second order. If the first-order perturbation fails to satisfy (47), the second order will not correct this. At the third order there are only potential terms; then (48) will be satisfied through third order if E_3 is the negative of E_1. This is our reason for preferring the third-order terms calculable with our perturbed functions already obtained to examining higher second-order terms. Rough calculation of Table III is compatible with this conjecture. For higher orders of perturbation, kinetic terms will enter only on even order, but there will be a variety of potential terms. In this formulation, it is possible to satisfy (48) at the equilibrium, even possible that (47) be generally satisfied.

A particularly attractive domain for application of the extended electrostatic model is in the estimation of the level splitting of partially occupied shells of complexes. Here the availability of isoelectronic sequences offers a possibility of eliminating or reducing the effect of uncertainties in the numerical values of uniform field polarizabilities. The isoelectronic polarizability relationships found by Pauling[20] in early work appear to be confirmed by recent calculations for large ions.

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