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Comments

Association Times of Counterions to Polyelectrolytes in Solution

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In a recent paper Manning¹ studied counterion flow in polyelectrolyte solutions under the combined influence of an external electric field and the electrostatic potential of a polyion and discussed the work of Huizenga *et al.*² on the electrolytic conductance of polyelectrolytes, interpreted by them on the assumption of counterion binding. Manning then made the following comment on a paper by two of us³: "Thus, the failure of Lifson and Jackson to find, in the absence of an external field, a long time of association of a counterion, considered as a Brownian particle, with an individual polyion does not mean, as we have seen, that the data of Huizenga *et al.* cannot be accounted for by electrostatic forces."

This statement confuses two distinct issues. Wall and his associates^{2,4,5} performed different kinds of measurements. One was the ionic conductance of Na⁺ counterions in polyelectrolyte solutions, which was found very low as compared with ionic conductance of Na⁺ in simple electrolytes. This reduction of mobility was attributed by them to counterion binding by the macroions. Another experiment involved the transference of radioactive tracer counterions across a frit in an otherwise homogeneous solution. They found the tracer ions to migrate both from the cathode to the anode and from the anode to the cathode across the frit. They attributed this phenomenon to a very long time of binding of the Na⁺ to the carboxyl ions, of the order of minutes.⁴

Now, Manning¹ did not discuss at all the problem of long times of association, while Lifson and Jackson³ studied this problem in particular and actually deduced that neither ion binding, which has an association time of $<10^{-8}$ sec, nor the entrapment of the counterion in the electrostatic potential of the macroion, which has an "escape time" of $<10^{-3}$ sec, could account for such long association times.

We feel that correcting Manning's comment is worthwhile, because even though almost two decades have passed since Wall's tracer experiments were published, there is still no satisfactory explanation for the phenomenon of migration of counterions for long times and distances both towards cathode and anode directions.

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³ S. Lifson and J. L. Jackson, *J. Chem. Phys.* **36**, 2410 (1962).

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Reply to the Comment of Jackson, Lifson, and Coriell

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The criticism of Jackson, Lifson, and Coriell is well taken. For the sake of clarity, however, I wish to point out, first, that the remark quoted by them was only incidental to my paper; second, that we all agree¹ that the problem to which I addressed myself, namely, the mobility of the counterion (sometimes negative!), was correctly solved.

¹ S. Lifson (informal discussion).

Convergence Properties of Certain Formulas for Multicenter Electron Repulsion Integrals Obtained from the Bipolar Expansion of r_{12}^{-1} *

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Recently, formulas for multicenter electron repulsion integrals over Slater-type atomic orbitals (STO's) were obtained via the bipolar expansion of r_{12}^{-1} in terms of

spherical harmonics and generalized Laguerre polynomials.¹ Here we point out that these formulas have the nature of asymptotic expansions, that they are divergent, and we indicate where in the derivation the transition to a divergent expression occurs.

The SBR¹ formula [Eq. (5.4) of SBR] for multi-center STO electron repulsion integrals is an infinite sum, each term of which involves the product of two overlap-type integrals and a generalized Laguerre polynomial. The convergence of the sum depends on the behavior of these factors for large values of the summation indices n_1 and n_2 . The Laguerre polynomial, for large n , goes like²

$$L_n^\alpha(x) \sim n^{\alpha/2-1/4} \pi^{-1/2} x^{-\alpha/2-1/4} \exp(\frac{1}{2}x) \times \cos[(4nx + 2\alpha x + 2x)^{1/2} - (\frac{1}{2}\alpha + \frac{1}{4})\pi],$$

as $n \rightarrow \infty$. (1)

The behavior of the overlap-type integrals is difficult to obtain for two-center charge distributions, but relatively easy for one-center distributions. One would expect the two-center overlap integrals with STO's to have a similar dependence on n as the one-center overlaps. That dependence is

$$\sigma_{NLM}^n(Za) \sim (-1)^{M+n} (2n)^N (Za)^{-2n-L} \exp[-\frac{1}{4}(Za)^2],$$

as $n \rightarrow \infty$, (2)

where σ_{NLM}^n is defined³ by SBR Eq. (5.16). The Z is an "orbital exponent" and a is an adjustable parameter set equal to Z^{-1} by SBR. When Eqs. (1) and (2) are substituted into SBR Eq. (5.19) for the two-center Coulomb integral (the convergence properties of which we assume typify the general four-center integral),

$$[AQ_a | BQ_b] = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \Omega_{n_1 L_a M_a n_2 L_b M_b} \times \sigma_{N_a L_a M_a}^{n_1} \sigma_{N_b L_b M_b}^{n_2},$$
 (3)

and SBR Eqs. (1.26), (1.22), (1.16), and (1.15) are taken into account, the general term in Eq. (3) can be shown to have the asymptotic form, valid for large n_1 and n_2 ,

$$\sum_{L=|L_a-L_b|}^{L_a+L_b} K n_1^{N_a} n_2^{N_b} [-\frac{1}{4}Z_a^2(a_1^2+a_2^2)]^{-n_1} \times [-\frac{1}{4}Z_b^2(a_1^2+a_2^2)]^{-n_2} [n_1+n_2+\frac{1}{2}(L_a+L_b-L)-1]^{L/2} \times [n_1+n_2+\frac{1}{2}(l_1+l_2-L)-1]! \cos(\text{an irrelevant mess}),$$
 (4)

where K is independent of n_1 and n_2 . As n_1 and $n_2 \rightarrow \infty$, the $[n_1+n_2+\frac{1}{2}(l_1+l_2-L)-1]!$ dominates, the magnitude of the term (4) clearly $\rightarrow \infty$, and Eq. (3) diverges. By inspection of Eq. (4), however, Eq. (3) has the form of an asymptotic expansion⁴ in inverse powers of $Z_a^2(a_1^2+a_2^2)$ and $Z_b^2(a_1^2+a_2^2)$.

The question naturally arises where in the derivation of SBR'S STO formulas did the expressions become divergent. The explanation involves a subtlety not too frequently encountered: an infinite series which cannot be integrated term by term. In the evaluation of the four-center STO electron repulsion integral, Eq. (5.1) of SBR, one first substitutes SBR Eq. (1.3) for r_{12}^{-1} and obtains the integral [cf. SBR Eq. (1.4)],

$$I = \int dV_1 \chi_{q_a}^*(\zeta_a \mathbf{r}_1) \chi_{q_b}(\zeta_b \mathbf{r}_{1B}) \times Y_{l_1 m_1}(\theta_1, \phi_1) J_{l_1 l_2 L}(r_1, r_2, R),$$
 (5)
$$= 2\pi^{-1/2} \int dV_1 \chi_{q_a}^*(\zeta_a \mathbf{r}_1) \chi_{q_b}(\zeta_b \mathbf{r}_{1B}) Y_{l_1 m_1}(\theta_1, \phi_1) \times \int_0^\infty dk j_{l_1}(kr_1) j_{l_2}(kr_2) j_L(kR),$$
 (6)

where we have taken $\mathbf{r}_1 = \mathbf{r}_{1A}$. (We discuss only $\int dV_1$, but the argument is equally valid for $\int dV_2$.) SBR first expand $j_{l_1}(kr_1)$ in generalized Laguerre polynomials, then integrate over dV_1 term by term, to obtain [cf. SBR Eqs. (5.5), (1.25), and (1.8)]

$$I = \sum_{n_1=0}^{\infty} 2\pi^{-1/2} \mathcal{S}(q_a, q_b, q_1) \int_0^\infty dk \exp(-\frac{1}{4}k^2 a_1^2) \times (ka_1)^{2n_1+l_1} j_{l_2}(kr_2) j_L(kR).$$
 (7)

It is the step

$$\int dV_1 \sum_{n_1} \rightarrow \sum_{n_1} \int dV_1$$

which is illegal for STO's. Examination of Eqs. (6) and (7) reveals that the function

$$I_2 = \exp(\frac{1}{4}k^2 a_1^2) \int dV_1 \chi_{q_a}^*(\zeta_a \mathbf{r}_1) \times \chi_{q_b}(\zeta_b \mathbf{r}_{1B}) Y_{l_1 m_1}(\theta_1, \phi_1) j_{l_1}(kr_1),$$
 (8)

has been expanded in a Taylor series in k . Apart from the $\exp(\frac{1}{4}k^2 a_1^2)$, I_2 is essentially a finite sum of the functions $G_{l_1 l_2 L}^{n_a n_b n_1}(k, R)$ which occur in the Fourier transform of a two-center charge distribution.⁵ Since the G 's have logarithmic singularities at $k = \pm i(\zeta_a + \zeta_b)$ (in the one-center case, the singularities are poles), the power series for I_2 diverges when $|k| > \zeta_a + \zeta_b$, and in particular, that part of the k integration from $\zeta_a + \zeta_b$ to ∞ in Eq. (7) has thus been evaluated incorrectly.

That SBR's formulas for STO multicenter integrals diverge does not rule out their possible usefulness. When the orbital exponents are all large, if the dominant part of the k integration comes from the region k less than the sum of the orbital exponents, then the formulas may be useful as asymptotic expansions.

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¹ L. S. Salmon, F. W. Birss, and K. Ruedenberg, *J. Chem. Phys.* **49**, 4293 (1968), hereafter referred to as SBR.
² M. A. Abramowitz and I. A. Stegun, Eds. *Natl. Bur. Std. (U.S.) Appl. Math. Ser. 55* (1964), Eqs. (13.2.9) and (13.5.14).
³ Note especially Eq. (5.17) of SBR for $\sigma_{N_e L_e M_e}^{m_e}$ apparently contains typographical errors.
⁴ See, for instance, A. Erdélyi, *Asymptotic Expansions* (Dover Publications, Inc., New York, 1956), p. 26, Eq. (2).
⁵ H. J. Silverstone, *J. Chem. Phys.* **48**, 4098 (1968), Eq. (30).

Comments on the Convergence Properties Observed by H. J. Silverstone and K. G. Kay

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In connection with further work on multicenter electron repulsion integrals we, too, had recently noted the divergence of our previously published expansions for four-center integrals between Slater-type atomic orbitals. On the other hand, the corresponding expansions do converge for Gaussian-type atomic orbitals; they are in fact finite. This circumstance seemed to suggest to us that the expansions for the STAO integrals would be asymptotically convergent, since the following argument can be made: For a given exponential charge distribution $\exp(-\zeta r)$, it is possible to find a Gaussian charge distribution $\exp(-\alpha r^2)$ such that, within a desired accuracy, both charge distributions can be set equal to zero for $r > R$, and $\exp(-\zeta r) < \exp(-\alpha r^2)$ for $r \leq R$, where R is appropriately chosen. Since it is possible to find a convergent expansion for the Gaussian charge distribution, the first terms of the corresponding expansion for the exponential charge distribution might be expected to approximate the integral within the desired accuracy.

We are appreciative that H. J. Silverstone and K. G. Kay have analyzed the problem in detail and demonstrated the asymptotic convergence.

Errata

Erratum: Classical Theory of Rotational Relaxation of Diatomic Molecules

[*J. Chem. Phys.* **47**, 4199 (1967)]

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Errors in plotting of the experimental relaxation times and collision numbers have been kindly pointed out by R. C. Amme.

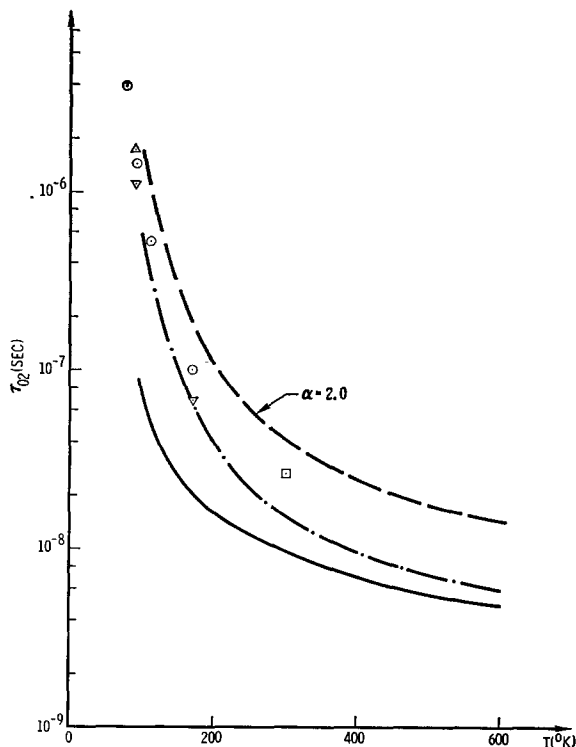


FIG. 3. Rotational relaxation times τ_{02} vs temperature. ---, p-H₂-He; ▽, Jonkman and Ertas; -·-, p-H₂-p-H₂; ○, Jonkman and Ertas; □, Geide; △, Van Itterbeck and Verhaegen; —, o-D₂-He.

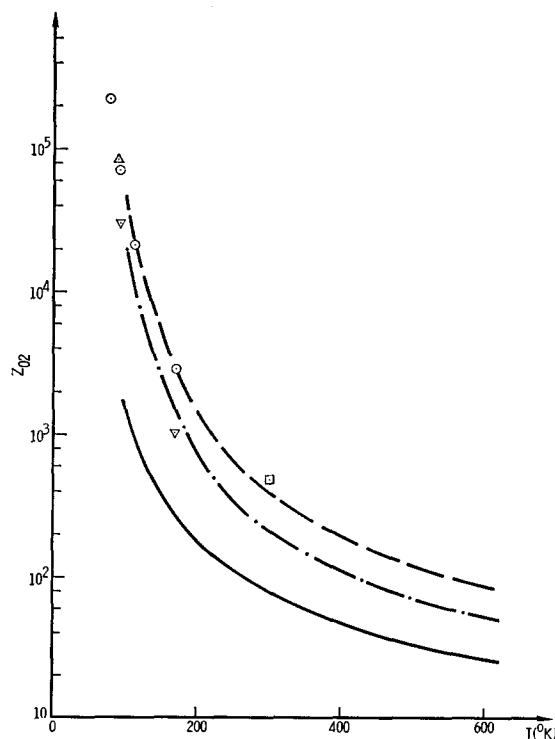


FIG. 4. Collision numbers Z_{02} vs temperature. ---, p-H₂-He; ▽, Jonkman and Ertas; -·-, p-H₂-p-H₂; ○, Jonkman and Ertas; □, Geide; △, Van Itterbeck and Verhaegen; —, o-D₂-He.