# *Molten Salt Chemistry*

EDITED BY **Milton Blander**
NORTH AMERICAN AVIATION SCIENCE CENTER
CANOGA PARK, CALIFORNIA

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# Introduction

During the last fifteen years, the technological uses of molten salts have rapidly become more important and research activity has accelerated and produced many important advances in our understanding of these media. This book was conceived in 1959, while I was still at the Oak Ridge National Laboratory. Although several notable short review articles have appeared,* they, of necessity, could not be as comprehensive as a collection of reviews of this sort and, consequently, much of the field has never been adequately reviewed. The purpose of this book is to provide a reference on molten salt chemistry and thus to review and call attention to some of the relatively new and significant work on fundamental aspects of this field.

The topics to be covered and the contributing authors were selected after many discussions with others, especially with Dr. Max Bredig, Dr. Roy F. Newton, and Dr. Warren Grimes of the Oak Ridge National Laboratory and with Professor George Scatchard of MIT and Professor Richard Laity of Princeton. Although initiated in 1961, the work on this book was not complete before I left the Oak Ridge National Laboratory in May of 1962. Four of the chapters were completed early (Klemm, Blander, Stillinger, and Ricci), and the first three of these needed major revisions by the time the later chapters were submitted. Revision of the chapter by Ricci was not considered necessary since inclusion of the more recent work would probably not lead to any significant change in this chapter. The dates of completion of the final forms of the chapters range from the latter part of 1961 to early in 1963.

Since the field does not encompass a single discipline, but is organized about the study of a particular class of materials, the chapters reflect different viewpoints. As a result, no attempt has been made to impose a uniform style on the chapters. Each chapter was intended to be a self-contained and critical review of the portion of the field covered and, in general, emphasizes what one learns about molten

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* (*1*) Laity, R., "Electrodes in Fused Salt Systems," in D. Ives and G. J. Janz, eds., *Reference Electrodes*, Academic Press, New York, 1961. (*2*) Janz, G. J., C. Solomons, and H. J. Gardner, *Chem Rev.*, **58**, 461 (1958). (*3*) Blomgren, G. E., and E. R. Van Artsdalen, *Ann. Rev. Phys. Chem.*, **11**, 273 (1960). (*4*) Bloom, H., and J. O'M. Bockris, "Molten Electrolytes," in J. O'M. Bockris, ed., *Modern Aspects of Electrochemistry*, No. 2, Butterworths, London, 1959.

salts rather than what one does with them. Consequently, the chapters emphasize results and theory, and the discussions of experiments have been minimized. An effort was made to provide as broad a view as possible of the fundamental work in the field and to list the most important references.

The chapters by Stillinger and by Levy and Danford on theory and structure should be of most interest to theoreticians; these contributors review the mathematically most sophisticated studies of this field. In my own chapter, I have attempted to logically organize knowledge of the thermodynamics of molten salt solutions. The chapter by Ricci provides, for the first time, an analysis and review of many of the enormous number of phase studies. Bredig has reviewed work on the interesting and unusual metal–metal salt solutions. The chapters by Smith and James cover much of the very precise and careful work on spectra and the chapter on transport properties by Klemm provides a discussion of a field which not only has important technological applications, but has provided and will continue to provide a rich field for future experimental and theoretical studies. The chapter by Bauer and Porter discusses the structure and interactions of species in salt vapors which provide a stringent test for physical theories of ionic interactions. Further, the deduction of thermodynamic properties of molten salts from vapor pressure measurements is dependent on a knowledge of the state of the vapor. The chapter on electroanalytical chemistry by Liu, Johnson, and Laitinen covers work on the important electrochemical research tools which have proven useful in analysis and can provide sensitive techniques for studying the kinetics of chemical reactions.

I gratefully acknowledge the help and encouragement I received at the Oak Ridge National Laboratory where most of my work on this book was done, and at the North American Aviation Science Center where it was completed. I am most grateful for suggestions concerning some of the manuscripts by Professor George Scatchard, Professor Richard Laity and Professor Ole Kleppa and for the continuing help and encouragement of Dr. Max Bredig.

There remain many unexplored areas and it is to be hoped that this book will provide one of the staging points for the next series of developments.

*Canoga Park, California* MILTON BLANDER
*July 22, 1963*

# Contributors

S. H. Bauer
*Department of Chemistry, Cornell University, Ithaca, New York*

Milton Blander
*North American Aviation Science Center, Canoga Park, California*

M. A. Bredig
*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

M. D. Danford
*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

David W. James
*Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

K. E. Johnson
*Sir John Cass College, London, England*

A. Klemm
*Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz, Germany*

H. A. Laitinen
*University of Illinois, Urbana, Illinois*

H. A. Levy
*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

C. H. Liu
*Polytechnic Institute of Brooklyn, Brooklyn, New York*

R. F. Porter
*Department of Chemistry, Cornell University, Ithaca, New York*

John E. Ricci
*Department of Chemistry, New York University, New York, New York*

G. Pedro Smith
*Oak Ridge National Laboratory, Oak Ridge, Tennessee*

Frank H. Stillinger, Jr.
*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*

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# Equilibrium Theory of Pure Fused Salts

FRANK H. STILLINGER, JR.
*Bell Telephone Laboratories, Incorporated,*
*Murray Hill, New Jersey*

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## I. Introduction

Inherent in the nature of fused salts are two fundamental complications which the theorist must understand and surmount. In the first place, these substances are representative members of the class of liquids, a state of matter whose microscopic structure and thermodynamic properties have always been difficult to predict quantitatively from the known character of the constituent molecules. In the liquid state, one has appeal neither to the structural regularity of crystalline solids, where atomic motions may be regarded as a superposition of running harmonic waves (normal vibrational modes for the lattice), nor to the situation characteristic of dilute gases, where collisional encounters are rare and occur predominantly between isolated molecular pairs. In common with gases, ordinary liquids have an essentially disordered nature over distances in the substance of macroscopic size. In this article it will become clear, however, that the positions of neighboring particles in liquids, and especially molten salts, are often indicative of a strong local ordering influence, or "structure," which is, in the last analysis, a direct result of the qualitative features of the force laws acting between the constituent particles.

The most obvious, and yet striking result of liquid disorder in the large (exempting the case of covalently bound glasses) is the property of fluidity. An adequate understanding of the liquid state must explain this ease of flow, with the seemingly contradictory fact of near-solid packing densities. The flow properties of liquids, vis-à-vis those of the other two states of aggregation, must reflect distinctive modes of molecular motion. These molecular motions in liquids are qualitatively unlike the separate collisions interrupting gas particle linear trajectories (with a well-defined free path length), or the multiply periodic lattice vibrations; they are instead a complicated Brownian motion. The rather small density change occurring upon melting of the solid therefore has a very profound effect on the collective aspects of molecular motion, and we anticipate that the local arrangement of the ions in salts also changes upon melting in a significant fashion to remain consistent with these modes of motion.

The second significant and difficult characteristic of molten salts is, of course, the fact that the constituent particles are electrostatically charged. The extreme range of the Coulomb potential energy, compared, for example, with the Lennard-Jones interaction often quoted for noble gas atom pairs, proved in the early years of theoretical chemistry to provide a classical mystery insofar as understanding the thermodynamic properties of electrolytic solutions was concerned. The resolution proposed in the pioneering work of Debye and Hückel (19) demonstrated lucidly the profound effect that these long-range forces produce. Specifically, the various measurable equilibrium properties of dilute electrolytes in non-electrolytic solvents cannot be expressed as salt concentration power series, as is the case for solutions of non-electrolytes.

Pure molten salts are perhaps the most concentrated electrolytic fluids obtainable by ordinary laboratory techniques. They are most certainly outside the range of applicability of the Debye-Hückel approach. That the extra electrostatic binding in an ionic assembly has primary significance for fused salts is clear from the very high melting and boiling points, as well as the large surface tensions at elevated temperatures measured for these substances. Obviously, the ultimate theoretical analysis of fused salts must explicitly acknowledge the existence of Coulomb interactions, and clarify their role in determining ionic motions and arrangements.

This article is intended to survey some of the existing theoretical approaches to the explanation of the equilibrium properties of pure fused salts. We shall not undertake to investigate the interesting field of transport processes such as electrical and thermal conduction, viscous dissipation, and diffusion, each of which demand establishment of a non-equilibrium state for experimental observation and measurement. However, an elucidation of the equilibrium molecular structure may well serve eventually as a large aid in providing an account of irreversible phenomena close to equilibrium. In addition to covering past work in the field, an effort will be made to point out novel theoretical relations and points of view which seem to merit future detailed examination.

As a preliminary to a review of the powerful Gibbs ensemble technique in equilibrium statistical mechanics, the nature of the forces acting between ions will be discussed at some length. Beside the somewhat trivial exercise of showing how the Coulombic ion–ion interactions arise from the detailed quantum-mechanical theory, it is instructive to analyze the nature of the other types of interactions that occur, and to emphasize the points at which the specifically chemical distinctions between ions of the different elements are important. The natural adjunct to such inquiry is recognition of the existence and nature of complex ions in the melt; unfortunately, limitations on a survey article of this sort prevent any but the most cursory acknowledgment of the fundamentals of modern structural inorganic chemistry, and of their value in predicting the properties of polyatomic species present in melts. On the other hand, it is necessary to stress that the ionic polarizabilities, which may be computed quantum-mechanically, are required for later discussion of the basic dielectric properties of fused salts.

The viewpoint in the following article is that approximate statistical theories of fused salts must be critically evaluated and understood, insofar as it proves feasible, in terms of their relations to and deductions from the rigorous (but often impractically complex) results of fundamental statistical mechanics. In this connection, the intention will be mainly to provide such justifications and criticisms on the basis of informal mathematical and physical intuition. It will soon become apparent to the reader that much remains yet to be accomplished in this field, especially in the way of carrying out detailed computational programs on the various theoretical analyses available at the time of this writing. The present survey will attempt to indicate not only the lines of past progress, but also the major theoretical stumbling blocks and weaknesses remaining.

## II. Forces Between Ions

The most fundamental characteristic of any assembly of molecules or ions, from the standpoint of statistical-mechanical theory, is the type of interactions operative between the constituent particles. To obtain a reasonably detailed account of these interactions and the corresponding forces, it is mandatory to use the notions of quantum mechanics. As a matter of historical fact, one of the early triumphs of wave mechanics in the hands of Heitler and London (32) was satisfactory explanation of chemical covalent binding forces, both qualitatively at first, and later with gratifying numerical agreement with experimental calorimetry and spectroscopy. Likewise, the attractive and repulsive "physical" forces acting between chemically saturated molecules received adequate explanation following London's recognition of the source of dispersion forces (47).

We shall begin this article on fused salts by providing a brief sketch of the quantum-mechanical foundation of intermolecular force theory. Special emphasis will be given to aspects peculiar to ionic particles. The major points to be stressed arise from the qualitative character of the interaction potentials, rather than in their precise numerical computation. It is very often the task of theory in this field to provide a fairly general functional form for intermolecular (interionic in our case) potentials. Subsequently, the remaining adjustable parameters are chosen best to fit some experimental data. A well-known example in this regard is choice of the Lennard-Jones potential depth and breadth parameters to fit measured second virial coefficients or gas viscosities for the noble gases. The main motivation for use of experimental information is the obvious fact that the complete quantum-mechanical theory is impossibly difficult to solve; the traditional sequence of approximation procedures (mentioned below) may be reliable in preserving many important gross features of the interaction potentials, but numerical imprecision is often demonstrably large.

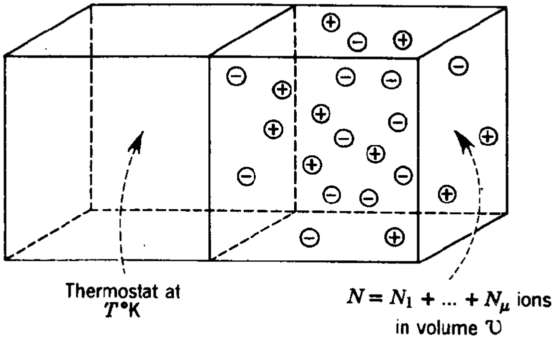

Fig. 1. The thermostated fused salt system in a container with rigid walls.

The molten salt microphysical situation for which we seek a description is a set of ions in a suitable container which, for our purposes, may be thought of as comprising impenetrable walls of a rectangular box (see Fig. 1). Since we ultimately desire to investigate states of thermodynamic equilibrium, it will be necessary to bring this system into thermal contact with a large heat reservoir, or thermostat, characterized by absolute temperature $T$. It will be presumed that temperature and over-all density are chosen such that the final thermodynamic states of interest are fluid phases, with intensive properties such as local density constant from point to point within each fluid phase. Gravitational effects are significant only insofar as they constrain the denser liquid phase, in a system containing coexistent liquid and vapor, to occupy the bottom of the container.

The individual ions are, of course, composed of orbital electrons surrounding essentially point nuclei. The total electronic and nuclear charges exactly cancel, to leave the entire fused salt system uncharged as a whole.

For a single pure salt whose constituent ions are monatomic, there are just two types of point nuclei which ultimately will form cations and anions. Denote their charges by $Z_+e$ and $Z_-e$, respectively, with positive integers $Z_+$ and $Z_-$ the atomic numbers, and $e$ the protonic charge. If there are $N_+$ and $N_-$ of each of these types of nuclei, then the system must contain precisely $M = N_+Z_+ + N_-Z_-$ electrons.

Except in the case of nuclei with the very lowest atomic numbers, electrons near these nuclei (the inner "core electrons") will be moving with relativistic velocities. It would be strictly proper, therefore, only to describe the entire nuclear and electronic system by means of a relativistic wave mechanics, i.e., the Dirac four-component matrix equation (63). It is also well known that these rapidly moving electrons, as a result of their relativistic character, are subject to spin-orbit couplings. One recognizes a fortunate circumstance, though, that ordinarily these relativistic effects do not explicitly enter into computation of intermolecular forces. Since they are primarily confined to the inner orbital electrons which are very little affected by the presence of neighboring ions, one may confidently use a completely nonrelativistic quantum theory for intermolecular force calculations. In other words, the absolute error of relativistic origin has virtually no direct effect on intermolecular forces. It would be a mistake to suppose, however, that simultaneously other properties of the ions will be appropriately described, but this fact is of no concern in the present context.

Consequently, we assume that the Schrödinger equation is an adequate formulation of electron and nuclear mechanical motion. The interaction portion, $U$, of the Hamiltonian operator now consists entirely of the Coulomb potentials for each pair of elementary particles. We split $U$ into a portion strictly involving only nuclear coordinates, $U_n$, and the remainder, $U_e$, dependent as well upon positions of the electrons:

$$\begin{aligned} U &= U_n + U_e \\ U_n &= \sum_{i<j=1}^{N_+ + N_-} \frac{Z_i Z_j e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \\ U_e &= \sum_{i<j=1}^{M} \frac{e^2}{|\mathbf{s}_j - \mathbf{s}_i|} - \sum_{i=1}^{M} \sum_{j=1}^{N_+ + N_-} \frac{Z_j e^2}{|\mathbf{r}_j - \mathbf{s}_i|} \end{aligned} \tag{1}$$

Position vectors $\mathbf{s}$ refer to electrons, $\mathbf{r}$ to nuclei.

A major simplification in the interatomic force problem results by use of the Born-Oppenheimer separation (11). The nuclei are sufficiently massive by comparison with the electrons that instantaneously their relatively sluggish motions (even at molten salt temperatures) may be disregarded in solving the quantum-mechanical electron problem. Thus the nuclei are regarded as providing a virtually time-independent force field in which the electrons move;

the "fixed" positions $\mathbf{r}_1 \ldots \mathbf{r}_N (N = N_+ + N_-)$ of these nuclei therefore adopt the role of parameters (rather than true quantum-dynamical variables) upon which the eigenfunctions and eigenvalues of the $M$-body electron problem implicitly depend. The small error in the Schrödinger equation eigenenergies as a result of this separation is known to be of the order of the square root of the electron to nuclear mass ratio (36).

One therefore considers a reduced, or Born-Oppenheimer, wave equation for the $M$ electrons:

$$\mathbf{H}\psi(\mathbf{s}_1 \ldots \mathbf{s}_M) = E\psi(\mathbf{s}_1 \ldots \mathbf{s}_M) \tag{2}$$

$$\mathbf{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{M} \nabla_i^2 + U_e(\mathbf{s}_1 \ldots \mathbf{s}_M)$$

$\hbar$ is Planck's constant divided by $2\pi$, and $m_e$ is the electron mass. Nuclear positions are implicit in both $E$ and $U_e$. The $M$ electrons, of course, have spin, but in writing the wave function $\psi$, as in equation 2, the spin coordinates have been suppressed in view of the fact that the Hamiltonian is spin independent. It is to be understood that $\psi$ is normalized and conforms to the Pauli principle; that is, $\psi$ must be antisymmetric with respect to simultaneous interchange of configuration and spin coordinates for any electron pair.

Presuming that it is possible to determine the ground-state energy, $E_0$, from equation 2 as a function of nuclear coordinates, and since electronic excitations are usually not important for molten salts, the interionic potential energy function, $V_N(\mathbf{r}_1 \ldots \mathbf{r}_N)$, for the molten salt will be taken to be

$$V_N(\mathbf{r}_1 \ldots \mathbf{r}_N) = E_0(\mathbf{r}_1 \ldots \mathbf{r}_N) + U_n(\mathbf{r}_1 \ldots \mathbf{r}_N) - E^\infty \tag{3}$$

The constant $E^\infty$ is the value of $E$ for infinitely separated nuclei, where the quantum state amounts to non-interacting ions. Consequently, $V_N$ vanishes for this separated configuration. The nuclear motion subsequently may in principal be obtained from the *classical* equations of motion for these $N$ particles, with interaction energy $V_N$. The positions of the various ions in the actual system of interest are then identified at any instant with the coordinates $\mathbf{r}_1 \ldots \mathbf{r}_N$.

With a specific nuclear (ionic) configuration, the $M$-electron wave function $\psi(\mathbf{s}_1 \ldots \mathbf{s}_M)$ has properties which satisfy a fundamental theorem of molecular quantum theory. This theorem, which is useful in understanding the nature of forces between the ions of a salt, was discovered independently by Hellmann (33) and Feynman (22). It states simply that the force on each nucleus is precisely the same as would be computed on the basis of classical electrostatics, from a charge density given by the fixed nuclear charges and the local electronic charge density, $\rho_e(\mathbf{r})$. This latter is directly obtained from $\psi$ by integrating $|\psi|^2$:

$$\begin{aligned}\rho_e(\mathbf{r}) &= -e\sum_{i=1}^{M}\int d^3\mathbf{s}_1\ldots d^3\mathbf{s}_M\delta(\mathbf{r}-\mathbf{s}_i)|\psi(\mathbf{s}_1\ldots\mathbf{s}_M)|^2 \\ &= -eM\int d^3\mathbf{s}_2\ldots d^3\mathbf{s}_M|\psi(\mathbf{r}\mathbf{s}_2\ldots\mathbf{s}_M)|^2\end{aligned} \tag{4}$$

where the fact that all electrons must be regarded as indistinguishable has been used. Having computed the forces by this scheme, $V_N$ follows by integration, subject to the vanishing of this latter quantity for infinite separation. Isolated ions of the smaller atomic number elements have spherically symmetric charge distributions in their ground states (closed shells of electron orbitals). If these distributions were preserved separately for each ion, regardless of position, electrostatics then would claim, by way of the Hellmann-Feynman theorem, that $V_N$ would be precisely a sum of Coulombic contributions for the ion-charge pairs if all distances were not so small as to allow ion electron cloud overlaps. Since we shall see this is an oversimplification for $V_N$, ion charge distortions must be important. A significant value of the Hellmann-Feynman theorem is its recognition that characteristically nonclassical features such as electron spin, and particle indistinguishability (the Pauli principle) have only an indirect effect on intermolecular forces, by the way in which they affect $\rho_e(\mathbf{r})$ through $\psi$.

Let us first examine the interaction $V_{\gamma\delta}(r)$ between an isolated pair of ions, ion 1 of species $\gamma$ and ion 2 of species $\delta$, with internuclear separation $r$. When $r$ is very large, $V_{\gamma\delta}$ vanishes, and in this configuration the electron density around each ion is spherically symmetric. We distinguish two cases: *(1)* $r$ small enough so significant overlap of electron clouds occurs, and *(2)* $r$ moderately large to prevent overlap, but still sufficiently small to produce mutual electron cloud polarizations. For the former, $r$ is so small that the set of orbital electrons for both ions are being forced into the same region of space. The Pauli exclusion principle assures that electrons of the same spin, at least, will avoid one another, so as to displace the electron clouds outward from the region of overlap between nuclei 1 and 2. Furthermore, an attempt to crowd many electrons into a common region (the overlap region) would produce a considerable rise in electron kinetic energy for all electrons involved, regardless of spin. Both effects therefore tend to force electrons out of the region between the nuclei. In this event, the Hellmann-Feynman theorem implies that the nuclei should experience a very powerful repulsion.

Several numerical calculations have been carried out on this repulsive energy for the noble gases (3,62). Since most monatomic ions have completed outer valence shells of electron orbitals (noble gas configurations), it is reasonable to suppose that a qualitatively similar result holds for ion overlap repulsions. It is generally found that this contribution to $V_{\gamma\delta}(r)$ may be represented well by a very rapidly decaying exponential function, with large multiplicative coefficient,

$$V_{\gamma\delta}(r) \rightarrow A\ \exp(-Br) \qquad (r\ \text{small}) \tag{5}$$

It should be noted that Born and Mayer (10) have been reasonably successful in explaining ionic crystal binding energies, by use of this exponential type of repulsive interaction.

The computional procedures used in obtaining results of type 5 have amounted to first- or second-order quantum-mechanical perturbation theory, where the perturbation is the sum of electron–electron Coulomb repulsions for pairs of electrons, one member of which is included in the electron cloud of ion 1, the other in the cloud of 2. Typically, it is necessary even in the most accurate procedure possible here to utilize properly antisymmetrized product wave functions, built up from only single-electron wave functions of the self-consistent field type, as the set of unperturbed basis functions.

It is the very rapidly rising repulsive portion for $V_{\gamma\delta}(r)$ computed in this way which allows the concept of a meaningful collision diameter for the ion pair 1,2. The typical values of A and B obtained are so large that the fractional change in $r$ causing the value of expression 5 to change from $kT$ to $2kT$ ($k$ is Boltzmann's constant) at molten salt temperatures is very small. In other words, function 5 appears to be almost vertical.

On account of this rapidly rising feature of the repulsive energy inside the collision diameter, it has often been found advantageous to replace the exponential decay form by a function qualitatively similar, but with mathematical properties tending to simplify specific problems. We mention in this connection two common choices. The first is the inverse twelfth (or more generally inverse $n$th) power law, appearing in the well-known Lennard-Jones potential function. Secondly, a rigid sphere interaction may be employed as the logical limit of rapid onset of repulsion.

The only explicit manner in which the nonvanishing ionic charges are reflected in the parameters of equation 5 is by their effect on the self-consistent single-electron orbitals used to compute relevant matrix elements in the perturbation theory. A net positive charge for cations implies less expanded orbitals than for the corresponding isoelectronic noble gas; negative anions have more expanded orbitals. The resulting change in the collision diameter for ion pairs can be quite marked. In the case of the analogs—two-electron hydride ion and helium atom, for example—the crystal radii are, respectively, 2.08 and 0.93 A. (56).

In the second case of intermediate $r$, where there is negligible electron cloud overlap, some important contributions to $V_{\gamma\delta}(r)$ are rather more subtle. Once again quantum-mechanical perturbation theory is the tool necessary for detailed calculations. The perturbation now, though, is taken to be the operator $H'$ corresponding to interaction between the various charge multipoles instantaneously present at the two ions. Specifically, we choose parallel coordinate systems centered at each nucleus with $z$ axes in the direction $\mathbf{r}$, so

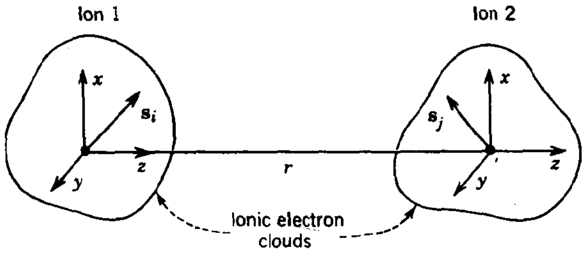

Fig. 2. Coordinate systems used in the multipole interaction perturbation $H'$. Electrons in the ionic "clouds" are located by displacement vectors $\mathbf{s}$ giving positions relative to the respective nuclei.

the $x$ and $y$ axes lie in planes normal to $\mathbf{r}$ through the respective nuclei, as in Figure 2. When the electrons in the respective ionic clouds are specified in position by their components $x_i$, $y_i$, and $z_i$ of displacement $\mathbf{s}_i$ from the nucleus to which they are bound, $H'$ may be written as an inverse series in $r = |\mathbf{r}|$:

$$\begin{aligned} H' = {} & \left[\frac{(Z_\gamma - n_\gamma)(Z_\delta - n_\delta)e^2}{r}\right] + \left[\frac{(Z_\gamma - n_\gamma)e^2}{r^2}\sum_{j=1}^{n_\delta} z_j \right. \\ & \left. - \frac{(Z_\delta - n_\delta)e^2}{r^2}\sum_{i=1}^{n_\gamma} z_i\right] + \left[\frac{e^2}{r^3}\sum_{i=1}^{n_\gamma}\sum_{j=1}^{n_\delta}(x_i x_j + y_i y_j - 2z_i z_j)\right] \\ & + \left[\frac{(Z_\gamma - n_\gamma)e^2}{r^3}\sum_{j=1}^{n_\delta}(z_j^2 - {}^1/_2 x_j^2 - {}^1/_2 y_j^2)\right. \\ & \left. + \frac{(Z_\delta - n_\delta)e^2}{r^3}\sum_{i=1}^{n_\gamma}(z_i^2 - {}^1/_2 x_i^2 - {}^1/_2 y_i^2)\right] + 0(r^{-4}) \\ = {} & H'_{cc} + H'_{cd} + H'_{dd} + H'_{cq} + 0(r^{-4}) \qquad (6) \end{aligned}$$

Summation index $i$ has here been used only for the $n_\gamma$ electrons of the ion 1, and $j$ only for the $n_\delta$ electrons of ion 2.

The various terms in $H'$ may easily be recognized. The leading contribution, $H'_{cc}$, dropping off with inverse distance, is the Coulomb interaction operator between the two ions regarded as point charges. $H'_{cd}$, decreasing with distance by an extra $r^{-1}$ factor, represents the instantaneous electrostatic interaction of charge on one ion with the dipole moment of the other, as well as the reverse; the interaction again is that for point multipoles. Likewise, $H'_{dd}$, varying as $r^{-3}$, is a dipole–dipole term. The last explicitly indicated contribution is for the interaction of a point charge–point quadrupole variety, and is also an $r^{-3}$ perturbation. The neglected terms, $0(r^{-4})$, amount to charge–octupole, dipole–quadrupole, etc. interactions. When $r$ is not too small (greater than four or five ionic collision diameters), the multipole expansion converges sufficiently rapidly that neglect of these higher order terms is appropriate.

The unperturbed wave function for the $n_\gamma + n_\delta$ electrons may be taken as simply a product of the individual isolated ion wave functions; since overlap is assumed negligible, it is unnecessary to antisymmetrize the resulting product with respect to interionic electron permutations, in computing the necessary matrix elements. For ions of small atomic number, the isolated ion wave functions are spheri-