An Approach to the Calculation of High-Energy Displacement Reaction Yields

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Abstract: An attempt is made to calculate the reaction cross section for hot reactions of the type \( ZY + X \rightarrow ZX + Y \), where \( X \) and \( Y \) are isotopes. For this purpose, a model is assumed which permits a simple (classical) treatment of the three interacting particles. The reaction cross section \( \sigma(E) \) is obtained by averaging over initial conditions selected in a random manner, by the Monte Carlo method. The results are compared with those obtained by Karplus, et al., for reactions \( \text{H}_2(\text{D}_2) + \text{T} \rightarrow \text{H(D)T} + \text{H(D)} \) and with experiment. In all cases a good fit is obtained.

I. Introduction

Two different models have been used to investigate hot displacement reactions of the kind

\[
ZY + X \rightarrow \begin{cases} \text{ZX} + Y \\ \text{XY} + Z \end{cases} \tag{1.1}
\]

taking place in the gaseous phase. In this reaction \( X \) is a hot atom moving with relatively high translational energies (above the threshold energy of the reactions under consideration) and \( ZY \) is a molecule which will be assumed to be static. The two parts of the original molecule are atoms or groups of atoms which can be assumed, in a first approximation, to behave as a single particle.

Both models were used to compute the total reaction cross section \( \sigma(E) \) as a function of the kinetic energy of the hot atom.

The first model, suggested by Wolfgang and Cross\(^2\) and somewhat improved by Hsiung,\(^2\) is based on two principal assumptions: (a) the displacement reaction takes place by a direct billiard-ball-type collision between the projectile and the target atom; (b) the reaction will take place if the target atom receives kinetic energy exceeding the binding energy between itself and the radical, while the incident hot atom is left with less kinetic energy than its binding energy to the radical.

The second model, which is due to Karplus, Raff, Porter, and Sharma,\(^3\)-\(^7\) was originally proposed for the analysis of collision reactions in experiments with crossed molecular beams and was lately applied to hot-atom chemistry as well.\(^8\) Karplus and Raff computed differential cross sections for the reaction

\[
\text{CH}_3 + \text{K} \rightarrow \text{KI} + \text{CH}_3 \tag{1.2}
\]

using a semiempirical potential field which was originally proposed by Blais and Bunker.\(^9\)-\(^10\) Concerning the reaction

\[
\text{H}_2(\text{D}_2) + \text{T} \rightarrow \text{H(D)T} + \text{H(D)} \tag{1.3}
\]

Karplus, Porter, and Sharma calculated \( \sigma(E) \) using a semi-quantum mechanical potential field computed by

\[\text{(4) L. M. Raff and M. Karplus, ibid., 44, 1212 (1965).}\]
\[\text{(5) M. Karplus, R. N. Porter, and R. D. Sharma, ibid., 40, 2033 (1964).}\]
\[\text{(6) M. Karplus, R. N. Porter, and R. D. Sharma, ibid., 43, 3259 (1965).}\]
\[\text{(7) L. M. Raff, ibid., 44, 1202 (1966).}\]
\[\text{(8) M. Karplus, R. N. Porter, and R. D. Sharma, ibid., 45, 3871 (1966).}\]
\[\text{(9) H. C. Blais and D. L. Bunker, ibid., 37, 2713 (1962).}\]
\[\text{(10) H. C. Blais and D. L. Bunker, ibid., 39, 315 (1963).}\]

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Karplus and Porter. Lately this potential field was modified by Shavitt, Stevens, Minn, and Karplus, and using this potential field Shavitt has computed rate constants for the exchange reactions (I.3). Once given the potential field, the motion of each of the particles in this field is determined by the classical equations of motion and by the initial conditions.

The differences in the above two approaches reflect the different purposes for which they were devised. The first model aimed at examining whether the hot atom reaction is a simple displacement reaction resulting from a direct billiard-ball-type collision between the atoms X and Y. The criterion according to which this assumption was tested was the existence of an isotope effect in the two reactions

\[
\text{CH}_4(\text{D}_2) + T \rightarrow \text{CH}_4(\text{D}_2)T + \text{H(D)}
\]  

However, the model turned out to be an oversimplification and the calculations disagreed with the experimental results. It was therefore discarded by the authors themselves.

The second model had a much broader aim, namely to describe the reaction process fully and to determine a variety of properties found in experiment. The results were in good, and sometimes even excellent, agreement with experiment, but the computations involved were very lengthy and complicated.

The present work attempts to calculate the cross section for exchange reactions by assuming a model which permits a semi-analytic treatment of the behavior of the three particles involved in the reaction. This model is related to the one-dimensional model treated by Mazur and Rubin in that the potential field assumed is composed of cutoff potentials; however, the model is three dimensional and this extension obviously complicates the whole treatment. The computations involved are nevertheless comparatively simple and short. Another advantage of this model is that it can be used for a rather large variety of exchange reactions in which the radical is an atom or a group of atoms which can be considered as a single particle, and Y and X are isotopes. The model is tested by comparing the reaction cross section for the reaction (I.3) with those computed by Karplus and Porter, as well as with experiment. The comparison with experiment is through the reaction integral \( R \) defined as

\[
R = \int_0^\infty \frac{\sigma(E)}{E} dE
\]

The reaction integral for these two reactions has been determined experimentally by Seewald, Gersh, and Wolfgang.

In section II, a description of the model is given, including a description of the reaction process. The theoretical and the experimental results are compared in section III and the conclusions summarized in section IV.

II. The Model

1. The Coordinate System and Initial Conditions. Three particles, Z, Y, and X, take part in the reaction. We shall treat the reaction

\[
\text{ZY} + X \rightarrow \text{ZX} + \text{Y}
\]

where Z is the radical with a mass \( M \), Y is the target atom with mass \( m_y \), and X is the projectile with mass \( m_x \). The origin is assumed to be at the center of mass of the system ZY and the axis of the molecule to be along the \( z \) axis. The distance between Y and Z at time \( t = 0 \) is \( L \), and the projectile X is at the point \( R \), where \( R \) is given, and the two other spherical polar coordinates \( \theta \) and \( \psi \) which determine the direction of \( R \) are chosen at random (see Figure 1). Thus, at time \( t = 0 \), the position coordinates of the three particles are

\[
Z \left( 0, 0, \frac{m_x}{M + m_y} L \right)
\]

\[
Y \left( 0, 0, -\frac{M}{M + m_y} L \right)
\]

\[
X \left( R \sin \theta \cos \varphi, R \sin \theta \sin \varphi, R \cos \theta \right)
\]

The initial momenta of Z and Y are taken as zero. This assumption might influence the results at the very low part of the reaction zone, but its effect is negligible on the whole. As for the projectile, one finds that for a given initial kinetic energy \( E \), the momentum \( P \) takes the form

\[
P_x = P(\cos \theta \cos \varphi \sin \delta \cos \eta - \sin \varphi \sin \delta \sin \eta + \sin \theta \cos \varphi \cos \delta)
\]

\[
P_y = P(\cos \theta \sin \varphi \sin \delta \cos \eta + \cos \varphi \sin \delta \sin \eta + \sin \theta \sin \varphi \cos \delta)
\]

\[
P_z = P(-\sin \theta \cos \eta \sin \delta + \cos \theta \cos \delta)
\]

where

\[
P = (2m_x E)^{1/2}
\]

and the angles \( \delta \) and \( \eta \) are spherical angles fixing the direction of the vector \( P \) in a coordinate system in which \( R \) is in the direction of the \( z \) axis. These two angles are selected at random from their respective distributions as \( \theta \) and \( \varphi \).

We note that out of 18 initial conditions, 14 are fixed and 4 are determined at random. Of the latter, the two angles \( \varphi \) and \( \eta \) are chosen from a distribution between 0 and \( 2\pi \), \( \theta \) is selected from a distribution between 0 and \( \pi \) weighted by \( \sin \theta \), and \( \delta \) is selected from a distribution between \( \pi/2 \) and \( \pi \) weighted by \( 2 \sin \delta \cos \delta \).

(13) I. Shavitt, ibid., 49, 4048 (1968).
(17) D. Seewald, M. Gersh, and R. Wolfgang, ibid., 45, 3870 (1966).
\[ \delta \] The selection of \( \delta \) is accomplished by taking \( \cos \theta \) to be uniform \(-1 \) and \( 1 \) and finding \( \delta \) from this cosine value, and the selection of \( \delta \) is performed by taking \( \cos^2 \delta \) to be uniform between \( 0 \) and \( 1 \) and calculating \( \delta \) from the negative square root of \( \cos^2 \delta \).

2. The Potential Energy Field. As far as the coordinate system and the initial conditions are concerned, we have seen that \( Y \) and \( Z \), the two components of the original molecule, were treated symmetrically. In order to preserve this symmetry in describing the reaction above that plane will lead only, if at all, to the reaction \( \text{reaction 11.4} \), i.e., if the collision happens beneath that plane, the only resultant reaction will be \( \text{reaction 11.5} \) (see Figure 2). Both are estimated from the respective Morse potentials. \( \rho_y \) fixes the region of repulsion between \( Z \) and \( Y \) and is estimated from the Morse potential as well. The depths of the potential wells \( V_{\alpha x}, \ V_{\alpha y}, \) are taken to be dependent only on the initial energy \( \mathcal{E} \), and the results are multiplied by \( \frac{m_y}{m_x + m_y} \).

\[
V(r_x) = V_y (1 - e^{-\omega_y(r_y - r_0)}) - V_{\alpha y} \quad \text{(II.11)}
\]

\[
V(r_y) = V_x (1 - e^{-\omega_x(r_x - r_0)}) - V_{\alpha x} \quad \text{(II.11\')]}
\]

We assumed that \( Y \) and \( X \) are isotopes; therefore the two Morse potentials are identical and yield \( R_x = R_y \) and \( V_{\alpha x} = V_{\alpha y} \). As for \( V_{\alpha y} \), it is assumed in that special case to be equal to \( V_{\alpha x} \). This choice of \( V_{\alpha} \) means that as long as the fourth term in the potential field (eq II.6) is ignored, the saddle point region which appears in every potential energy surface is not apparent yet. It therefore turns out that the only term responsible for this saddle point region is the fourth term, i.e., the term that yields the repulsion between \( X \) and \( Y \). The distance \( \rho_{xy} \) which appears in (II.10) is assumed to be energy dependent and will be determined by the equation:

\[
V(r_{xy}) = \frac{m_y}{m_x + m_y} \mathcal{E} = 0 \quad \text{(II.12)}
\]

where \( V(r_{xy}) \) is chosen to be of the form

\[
V(r_{xy}) = E_{ax} e^{-2\alpha (r_{xy} - r_{0})} \quad \text{(II.13)}
\]

In this potential \( \alpha \) is identical with \( \alpha_{ax} \) which appears in the Morse potential (II.11\'}). The distance \( r_{0} \) is defined as the closest approach between \( X \) and \( Y \) in the linear configuration \( Y-Z-X \) for which a reaction is still not possible. The reason for considering the linear configuration originates in the fact that the minimum-energy path lies entirely in this configuration. Thus, if \( X \) succeeds in approaching \( Y \) in the linear geometry up to a distance that is smaller than \( r_{0} \), then a reaction does occur. This closeness of approach can be achieved only if the reduced particle \( X-Y \) has, in the respective center-of-mass system, a kinetic energy equal to or larger than \( E_{ax} \). Since at time \( t = 0 \) the only particle possessing kinetic energy is the projectile and since the minimum energy required for performing the reaction is \( E_{ax} \) (the threshold energy), we can easily derive the connection between \( E_{ax} \) and \( E_{ax} \):

\[
E_{ax} = E_{ax} \frac{m_y}{m_x + m_y} (+ M)
\]

We notice that whereas \( \alpha \) and \( E_{ax} \) are well determined, \( r_{0} \) is not and will be computed by "trial and error."

It remains to deal with \( \rho_{xy} \) which determines the region of repulsion between \( X \) and \( Y \). This distance is the second energy-dependent parameter and will be extracted from the equation:

\[
V(r_x) = \frac{m_y}{M + m_x} \mathcal{E} = 0 \quad \text{(II.15)}
\]

where \( V(r_{0}) \) is given by eq II.11\'.

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For a given initial energy $E$, the potential field in the linear geometry is shown in Figure 2.

We notice that the potential field defined is composed of cutoff potential terms. However, in order to conserve the soft nature of the interaction between the hot particle and the molecule, those components of the potential with which the hot atom may interact while still in possession of its initial kinetic energy $E$ were made energy dependent. This requirement brought into that category the radius of repulsion between X and Y, i.e., $p_{xy}$ and the radius of repulsion between X and Z, viz. $p_{x}$.

3. The Reaction Process. In order to describe the reaction process we shall refer to the linear configuration. Since the potential energies in the different regions are constant, the relative motion of the three particles can be characterized by a rectilinear motion of the configuration point inside the different regions of the $r_{x}$, $r_{y}$ space. The transformation from the system of three "linear" particles to the configuration point system is accompanied by transformation from the rectangular coordinates system $(r_{x}, r_{y})$ to another rectangular system $(S_{x}, S_{y})$ where the distances $r_{x}$ and $r_{y}$ are skewed. The transformation from $(r_{x}, r_{y})$ to $(S_{x}, S_{y})$ is

\[ S_{x} = r_{x} + \frac{m_{y}}{m_{x} + m_{y}} r_{y} \]
\[ S_{y} = \frac{1}{M + m_{y}} [m_{y} M(m_{x} + m_{y} + M)]^{1/2} r_{y} \]  

As a result of this transformation, the five lines which define the potential energy surface, $r_{x} = \rho_{x}$, $r_{x} = R_{x}, r_{y} = \rho_{y}, r_{y} = R_{y}$, and $r_{y} = \rho_{xy} - r_{x}$ transform into the lines

\[ S_{x} = \frac{1}{M + m_{y}} \left( m_{y} M(m_{x} + m_{y} + M) \right)^{1/2} r_{x} \]
\[ S_{y} = \frac{1}{M + m_{y}} \left( m_{y} M(m_{x} + m_{y} + M) \right)^{1/2} r_{y} \]
\[ S_{y} = \frac{1}{M + m_{x}} \left( m_{x} M(m_{x} + m_{y} + M) \right)^{1/2} r_{y} \]
\[ S_{y} = \frac{1}{M + m_{y}} \left( m_{y} M(m_{x} + m_{y} + M) \right)^{1/2} r_{y} \]
\[ S_{y} = \frac{1}{M + m_{x}} \left( m_{x} M(m_{x} + m_{y} + M) \right)^{1/2} r_{y} \]

respectively (see Figure 3a and b).

4. Computation of the Total Cross Section. If $R$ is the initial distance between X and the center of mass of the two particles YZ and if $P(E, \theta, \phi, \delta, \eta)$ is the probability of obtaining a reaction when the initial energy of the projectile is $E$ and the initial angles are $\theta$, $\phi$, and $\eta$, then the total reaction cross section is given in the form

\[ \sigma(E) = \pi R^{2} \int_{h_{1}} \int_{h_{2}} \int_{h_{3}} P(E, \theta, \phi, \delta, \eta) \sin \theta \frac{d\theta}{2\pi} \frac{d\phi}{2\pi} \frac{d\delta}{2\pi} \frac{d\eta}{2\pi} \]  

where $h_{i}$, $\phi_{i}$, $\delta_{i}$, and $\eta_{i}$ $(i = 1, 2)$ are defined through the condition

\[ P(E, \theta, \phi, \delta, \eta) = \begin{cases} 1, & \theta_{1} \leq \theta \leq \theta_{2}, \phi_{1} \leq \phi \leq \phi_{2}, \\
\delta_{1} \leq \delta \leq \delta_{2}, \eta_{1} \leq \eta \leq \eta_{2} & \text{elsewhere} \end{cases} \]  

\[ \delta_{i} = \frac{\pi R^{2}}{2\pi} \int_{h_{i}} \int_{h_{2}} \int_{h_{3}} P(E, \theta, \phi, \delta, \eta) \sin \theta \frac{d\theta}{2\pi} \frac{d\phi}{2\pi} \frac{d\delta}{2\pi} \frac{d\eta}{2\pi} \]  

We recall that since $\rho_{x}$ and $\rho_{xy}$ are energy dependent, the two lines (ac) and (cd) are energy dependent too and change their positions accordingly.

For low energies, the skewed line (ac) is too close to the corner (e), and the configuration particle (which started at point A) hits this line and is reflected back into region I (see Figure 3a). As the energy increases, the line (ac) moves away from the corner (in such a manner that the angle of inclination is conserved), thus increasing the gap through which the particle is supposed to move into region II. The lowest energy for this is the case is $E_{o}$, the activation energy of the reaction (see Figure 3b).

The nonlinear, or the general, case was treated by a computer. To do this, a program was written computing the relative velocities and positions of the three particles following each of the two-body (hard-sphere) collisions. A reaction will occur if Y reaches the boundary of attraction before X does so, and if the translational energy $E_{x}$ of the reduced particle X-Z fulfills the condition

\[ E_{x} < \frac{V_{ox}}{\cos^{2} \delta} \]
The limits of the integration are functions of $E$ and of other magnitudes defining the reaction. The integration is, of course, performed numerically, using the Monte Carlo method. If, for a given $E$ and $R$, one gets from $N$ trajectories, $N_e$ reactions, then $\sigma(E)$ takes the form

$$\sigma(E) = \frac{\pi R_e^2 N_e(E, R)}{N} \quad (\text{II.20})$$

$\sigma(E)$ is, of course, independent of $R$.

### III. Calculation and Results

As concrete examples for testing the model, we chose the various $(H_2, H)$ systems, viz. $(H_2, T)$, $(D_2, T)$, and $(HD, T)$. The three systems differ only in the masses of the two atoms of which the hydrogen molecule is composed, whereas the potential field is assumed to be the same.

The total cross section $\sigma(E)$ was computed using the following numerical values: $V_0 = V_{ox} = V_{cy} = 4.4$ eV; $11 \alpha = 1.89 \text{Å}^{-1}$; $11 R = 3 \text{Å}$; $L = 0.75 \text{Å}$; $11 R_e = R_p = 1 \text{Å}$; $r_0 = 0.4 \text{Å}$; $r_0 = 0.85 \text{Å}$; $E_{ax} = 0.21$ eV. The values of $r_0$ and $E_{ax}$ were determined using the experimental value of the threshold energy $E_a$ for the reaction

$$\text{H}_2 + T \rightarrow \text{HT} + \text{H}$$

found by Kuppermann and White, $^{19}$ viz., $E_a = 0.33$ eV. Since the same values of $E_{ax}$ and $r_0$ were used for all the systems, it is possible to derive the threshold energy for the other reactions under discussion by the use of eq II.14. Thus, for the reaction

$$\text{D}_2 + T \rightarrow \text{DT} + \text{D}$$

the value of $E_a = 0.30$ eV is derived; for the reaction

$$\text{HD} + T \rightarrow \text{HT} + \text{D}$$

the value of $E_a = 0.27$ eV is derived; and for the reaction

$$\text{HD} + T \rightarrow \text{DT} + \text{H}$$

the value of $E_a = 0.40$ eV is obtained.

Although this model yields the threshold energies of the last three reactions, some caution must be taken since they were obtained neglecting the zero energy of the respective target molecules.

Figures 4 and 5 show the total reaction cross section $\sigma(E)$ as a function of $E$ for reactions 1.3. The curves are those computed by Karplus, et al., whereas the points represent the results of the present computations.

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Figure 4. Total reaction cross section as a function of tritium energy in the laboratory system for the reaction $\text{H}_2 + T \rightarrow \text{HT} + \text{H}$: curve, results of Karplus, et al.; points, present model.

Figure 5. Total reaction cross section as a function of energy for the reaction $\text{D}_2 + T \rightarrow \text{DT} + \text{D}$: curve, results of Karplus, et al.; points, present model.

Figure 6. Total reaction cross section as a function of energy: (____) $\text{HD} + T \rightarrow \text{HT} + \text{D}$; (---) $\text{HD} + T \rightarrow \text{DT} + \text{H}$.

We notice that the fit for the $(H_2 T)$ system is excellent. As for the $(D_2, T)$ system, it seems that the present calculation yields a somewhat larger cross section, but again the fit is good.

Concerning the comparison of the theory with experiment, the only experimental results relevant to these curves involve the concept of the reaction integral $R$. The ratio of reaction integrals $R_{HT}/R_{DT}$ predicted by the present model is 1.15; the theoretical calculation of Karplus, et al., yields the result of 1.37, while the experimental value is 1.15. $^{20}$ Another system for which the comparison with experiment is possible is the $(HD, T)$ system. Seewald and Wolfgang $^{20}$ found the ratio of the reaction integrals $R_{HT}/R_{DT}$ to be 0.62 ± 0.06. The present model yields the result of 0.89. The total reaction cross section as a function of energy for these reactions is given in Figure 6.

### IV. Conclusion

The model discussed in this paper enables the computation of hot displacement reaction cross sections for reactions of the type $ZY + X \rightarrow ZX + Y$, where $X$ and $Y$ are isotopes and $Z$ is an atom or group of atoms which is believed to behave as a single particle. The model follows the general lines of the model assumed by Karplus and Raff, but the different components of the Blais-Bunker potential used by Karplus and Raff are replaced by cutoff potentials, thus permitting a relatively simple treatment of the three atoms $X$, $Y$, and $Z$, during the reaction process. In this sense the model is closely related to the kinematic model of Suplinskas. $^{21}$ However, the main difference between the present model and the kinematic model stems from the fact that part

(20) D. Seewald and R. Wolfgang, ibid., 46, 1207 (1967).

of the parameters determining the potential field, which governs the motion of the particles is assumed to be dependent on the initial energy of the hot atom X. Doing this we reproduced what the hot particle "sees" from the true surface while possessing its high initial energy. This assumption has fully justified itself, because in contrast to the kinematic model, the present model yields a good fit with the curve for the reaction \( \text{D}_2 + \text{T} \rightarrow \text{DT} + \text{D} \) computed by Karplus, et al., and also the right isotopic effect for the reactions \( \text{HD} + \text{T} \rightarrow \text{H(D)T} + \text{D(H)} \). For the respective isotopic ratio \( R_{\text{HT}}/R_{\text{DT}} \) we derived the value of 0.89, the experimental value is 0.62 \pm 0.06, and Suplinskas' value is 1.6.

The good fit obtained with the theoretical calculations of Karplus, Porter, and Sharma and with the different experiments indicates that the main repulsive interaction during the reaction process is between the hot atom and the atom to be replaced, \( \text{viz.} \), atom Y. The nature of this repulsion is not of a pure billiard-ball type; however, it is not of too soft a nature either, since, in contrast to the hard-sphere approximation, the energy-dependent hard-sphere approximation yields the correct results.

The two main features of this model consist (1) in its being easily handled since the calculations involved are short (about 5 to 10 min for each curve) and (2) in its applicability to a large variety of reactions, since the potential field assumed is constructed using the experimental value of the threshold energy for the reactions and other parameters derived from the Morse potential of the molecule ZY.

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The Isoelectronic Principle and the Accuracy of Binding Energies in the Hückel Method

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Abstract: In the Hückel and other methods, binding energies are calculated by subtracting the sum of orbital electronic energies for the molecule from the sum of orbital electronic energies for the separated atoms, and not considering the internuclear repulsion. Since this last may be several orders of magnitude greater than the binding energy, reasonable results could not be obtained without an approximate cancellation with another neglected term. It is shown that such a cancellation is a consequence of the isoelectronic principle (invariance of binding energy to change in atomic number of constituent atom). Numerical examples are given.

In a number of \textit{a priori} and semiempirical methods, of which the extended Hückel method\(^2\) is the best known, one calculates molecular binding energies by subtracting the electronic energy (sum of orbital contributions) of the molecule from the sum of the electronic energies of the atoms, without considering the internuclear repulsion. If we accept the argument that the parameterization in the method effectively simulates a Hartree–Fock calculation, the “electronic energies” are really sums of orbital energies. To get the true electronic energies of atom or molecule, one must subtract off in each case the interelectronic repulsion, which is being counted twice. Thus the above recipe will be valid if

\[ V_{\text{NN}} \approx V_{\text{ee}} - \sum A V_{\text{ee}} = \Delta V_{\text{ee}} \]

(1)

where \( V_{\text{ee}} \) and \( V_{\text{ee}}^A \) are the interelectronic repulsions (expectation values) for the molecule and for atom A, and \( V_{\text{NN}} \) is the internuclear repulsion.\(^1\) The binding energy may be orders of magnitude smaller than \( V_{\text{NN}} \). Thus the error in eq 1 must be small (\textit{i.e.}, of the size of the binding energy itself) if reasonable binding energies are to be obtained from a wave function which is reasonable in other respects. Below, we show\(^3\) that this is in fact true in general, being a consequence of the isoelectronic principle.

The proof is closely related to the derivation of a formula\(^4\) for calculating diamagnetic Shieldings in molecules, also starting from the isoelectronic principle. According to this principle, two isoelectronic species have the same binding energies if they differ only by a change by unity in a nuclear charge. The example of \( \text{CO} \) vs. \( \text{N}_2 \), is perhaps the best known; one can easily find others.\(^7\) Writing \( Z_B \) for the charge of nucleus B, we express this as

\[ (3) \text{ Note that it is the change in } V_{\text{ee}} \text{ from atoms to molecule which must be approximately equal to } V_{\text{NN}}, \text{not } V_{\text{ee}} \text{ itself as has sometimes stated.} \]


(7) J. Berkowitz, \textit{J. Chem. Phys.}, 30, 855 (1959); also cf. ref 5.

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