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Albert Sprague Coolidge and Hubert M. James

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The Approximations Involved in Calculations of Atomic Interaction and Activation Energies

ALBERT SPRAGUE COOLIDGE AND HUBERT M. JAMES, *Harvard University*

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The assumptions underlying the computation of interaction energy among several atoms, and especially of activation energies, have been analyzed and discussed for the case of small overlapping of the one-electron wave functions involved. Some formal justification has been found for several types of approximation which have hitherto been used without adequate examination. Computations of the energy of several three-electron systems are presented as material illustrating the applicability

of some of the assumptions to typical cases. It is concluded that in general any modification of the complete Heitler-London treatment of the system may lead to errors comparable in magnitude to the quantity to be computed. The so-called "semi-empirical method," which involves many such modifications, owes its success to a happy cancellation of errors, and, until some theoretical explanation of this cancellation is found, it must assume the status and responsibilities of a purely empirical method.

1. ANALYSIS AND DISCUSSION OF APPROXIMATIONS

THERE have recently appeared numerous papers¹ attempting to predict activation energies of simple chemical reactions, by a method which is essentially a generalization of that first applied by Heitler and London² to the problem of two hydrogen atoms, with certain additional approximations. The starting point was an article by London³ giving an equation for the reaction energy of a system containing three electrons in three orbits having spin degeneracy only. London does not give the derivation of his equation, and, although he states that it is an approximation, he does not discuss the nature or magnitude of the omitted terms. His equation has been extended to more electrons by Eyring and his collaborators, also without examination of the approximations involved. It seems very desirable to subject the whole method to a more careful study.

Analysis reveals that, as usually employed, the method of computing reaction energies between several atoms involves, from the theoretical point of view, the following assumptions:

(A) That a useful result could be obtained by a rigorous application of the H.-L. method, in-

tegrating the complete energy operator (as distinguished from the interaction or perturbation terms alone) over a function built up from the unperturbed atomic functions, and then subtracting the unperturbed energy.

(B) That each atom may be represented by one or more "bonding" electrons, having definite individual orbits. Electrons in inner shells, and even "non-bonding" electrons in the same shell, may be neglected.

(C) That the result of a computation based on assumptions (A) and (B) would differ only by small terms from that given by the London formula, or its appropriate extension.

(D) That, in the London formula, those terms which arise from the exchange of two electrons are the same as they would be if these two electrons and their corresponding nuclear charges were the only bodies present, while terms arising from permutations of more than two electrons are negligible.

(E) That the division of the binding energy of a molecule like H_2 into "coulomb" and "exchange" terms has some significance aside from the H.-L. approximate method of computation, so that values of the latter more accurate than those given by calculation can be estimated from spectroscopic binding energies.

Our primary interest lies in the last three assumptions, and we may dismiss the first two with brief mention. Assumption (A), as is well understood, is applicable if the interaction energy of the system is small in comparison with the energy required to raise the unperturbed system to the

¹ For example, Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931); Rollefson and Eyring, *J. Am. Chem. Soc.* **54**, 170 (1932); Sherman and Eyring, *J. Am. Chem. Soc.* **54**, 2661 (1932); Taylor, Eyring and Sherman, *J. Chem. Phys.* **1**, 68 (1933); Eyring, Sherman and Kimball, *J. Chem. Phys.* **1**, 586 (1933).

² Heitler and London, *Zeits. f. Physik* **44**, 455 (1927).

³ London, *Zeits. f. Elektrochemie* **35**, 552 (1929); see also *Sommerfeld Festschrift*, Hirzel, p. 104.

next lowest energy state of the same symmetry. To judge from results, this condition is not well met. The H.-L. method applied to H_2 at the equilibrium distance gives about two-thirds the proper binding energy; with Li_2 the result is worse, previous excellent agreement with experiment⁴ having been obtained by neglecting the inner electrons. Nevertheless the method is certainly useful as a qualitative guide, and presumably is more accurate for activation energies, as the internuclear distances are somewhat greater, and the perturbation smaller.

As to assumption (B), the approximate treatments of such problems, in which only spin degeneracy is assumed, agree that so long as triple exchanges are negligible non-bonding electrons should produce a repulsion. If, owing to directed valence, the bonding orbits overlap much more than the non-bonding, the repulsions may be small compared to the attractions; but the methods based on the London formula explicitly neglect directional effects. When assumption (E) is used to estimate "empirical exchange terms" the errors associated with assumption (B) may be partly cancelled. Thus, if one takes 90 percent of the total binding energy to represent the exchange term of the binding electrons for two atoms at a certain distance in the absence of a third atom, this will be numerically smaller than the "real" exchange term, because the repulsion of non-bonding electrons will have been included. On bringing up a third atom and using the London formula, one may expect this modification to result in a partial duplication of the effect of the non-bonding electrons, because they probably continue to repel, though to a different degree. These remarks do not necessarily apply to all the cases which have been treated, since orbital degeneracy is in general present, and in the presence of inner shells the triple exchange terms may be very important. For instance, in a treatment of Li_2 one of us⁵ has found that the non-bonding electrons of the inner shells exert an attractive effect in the $^3\Sigma$ state, this arising from the commonly neglected triple exchange terms.

It is to be noted that if the non-bonding electrons are to be eliminated from consideration

it is essential to use only the perturbation operator. A discussion of the approximation involved in the neglect of the other terms in the complete energy operator is to be found elsewhere;⁶ it is in many cases not unsatisfactory. The approximation of then neglecting non-bonding electrons can be treated by the methods indicated in the discussion of assumptions (C) and (D). The result of applying only the second of these approximations with operators involving atomic terms in the energy along with wave functions including only the bonding electrons, in a treatment like that of assumption (A) is quite different, and cannot be similarly justified. We shall not pursue the subject further, and in what follows shall consider only systems with one electron per atom.

Assumption (C) involves the justification of the London formula. For three electrons, the formula is

$$\epsilon = C - a - (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha)^{\frac{1}{2}}. \quad (1)$$

Here, ϵ is the interaction energy, C is the sum of the Coulomb terms of the three pairs of orbits, α, β, γ , are the corresponding exchange integrals, and a is a term involving a triple exchange. It seems to be generally believed that this formula (omitting the term a) can be obtained by applying the H.-L. treatment in full, and then throwing out all terms which would vanish if the three orbits were mutually orthogonal; that is, by regarding the lack of orthogonality as an accidental matter, of small importance. Thus Slater⁶ gives formally the complete solution, and upon discarding terms arising from non-orthogonality, gets an expression which is formally the same as London's. (It is in reality very different, since the terms which it contains involve the whole energy operator, while London's contain only the interaction operator.) That this view of the matter is definitely wrong, will become apparent as soon as one remembers that it is precisely because the orbits are not orthogonal that the H.-L. method succeeds in predicting binding. If all terms due to non-orthogonality are systematically rejected, then the exchange terms will come out positive and repulsion will result. Indeed, the whole basis of the Slater-Pauling theory is the exten-

⁴ Bartlett and Furry, *Phys. Rev.* **38**, 1615 (1931).

⁵ James, *J. Chem. Phys.* **2**, 794 (1934).

⁶ Slater, *Phys. Rev.* **38**, 1109 (1931).

sive overlapping of orbits, and in general orbits which largely overlap will be far from orthogonal. If the London formula (without a) is limited to cases of inappreciable overlapping, it will be useless for computing activation energies. It is possible, as we shall now show, to formulate an argument justifying its use under somewhat less rigorous restrictions. At the same time, we shall find similar justification for assumption (D).

It will be best to start with the two-electron problem. The London formula becomes

$$\epsilon = C + \alpha, \quad (2)$$

while the complete solution is (in Slater's notation)

$$W = [(ab/H/ab) + (ba/H/ab)]/(1+s^2), \quad (3)$$

where s is the integral $\int abdV$, and may be taken as a measure of the degree of overlapping, or of lack of orthogonality. For large separations, s will be small compared to unity; as the centers approach, it will grow, reaching values of the order of one-half in many problems at the equilibrium distance. We shall regard s as a small quantity, developing the discussion in terms of the powers of s to which the various magnitudes are comparable.

To convert (3) formally into (2), we must drop s^2 in comparison with 1, which we are apparently at liberty to do. In fact, however, this will involve an error comparable to the quantity which we wish to calculate. Let us write

$$W = W^\circ + \epsilon, \quad (4)$$

where W° represents the unperturbed energy. Now, ab is a solution of

$$H^\circ(ab) = W^\circ ab, \quad (5)$$

(H° being the unperturbed operator), so that the two terms in the numerator of (3) have for their principal parts W° and $s^2 W^\circ$, respectively, the first being therefore much the larger. By omitting s^2 in the denominator, we make an error of the order $s^2 W^\circ$. But, as we shall see, the whole binding energy is of the second order in s , so that we cannot begin by simplifying the denominator of (3). We must first apply the well-known device of splitting off the unperturbed energy, expressing the operator as the sum of H° and H' , the

latter containing only the perturbation terms. Owing to (5), we then get

$$W = W^\circ + [(ab/H'/ab) + (ba/H'/ab)]/(1+s^2), \quad (6)$$

where the expressions in the numerator are now exactly the C and α of (2).

The terms in H' are of the same general nature as those in H° (except for the Laplacian in the latter). $C = (ab/H'/ab)$ might therefore be expected to be comparable to $W^\circ = (ab/H^\circ/ab)$. True, it should be somewhat smaller, because the distances involved in H' refer to particles in different atoms, and are therefore larger than those in H° , referring to particles in the same atom; but the ratio should not be as small as s , for s in general goes down as the negative exponential of the interatomic separation, which enters H' only as the minus first power. By a similar argument, we should expect $\alpha = (ba/H'/ab)$ to be comparable with $(ba/H^\circ/ab) = s^2 W^\circ$. (In this case the distances involved in H' and H° are the same.) Actually, however, we find that C is much smaller than α , due to extensive cancellation of terms, so that the whole numerator in (6) is of the second order in s ; we may therefore pass to the London formula by dropping s^2 in the denominator, with an error of the order $W^\circ s^4$, or ϵs^2 , making ϵ numerically too large; this tends to compensate the error fundamental to the H.-L. method. It remains to find out why the cancellation among the terms of C is so much more effective than among those of α , so that we may make predictions for more complex cases which have not been actually computed. To this end we expand C and α (using a notation developed by one of us⁷ in a previous paper)

$$C = A/B - aa/B - A/bb + aa/bb;$$

$$\alpha = s^2 A/B - s[ab/B + A/ab] + ab/ab.$$

In a purely formal way, these expressions may be rewritten

$$\begin{aligned} C &= (A - aa)/(B - bb); \\ \alpha &= (sA - ab)/(sB - ab). \end{aligned} \quad (7)$$

This draws attention to the fact that each integral may be regarded as the total mutual energy of two electrical distributions, each of zero total

⁷ A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

charge. In the case of C , each distribution is so arranged that the diffuse negative charge very effectively screens the concentrated positive charge. The mutual energy of two such charges is therefore doubly small; *we have here the reason why the Coulomb term is at least two orders smaller than superficial analysis suggests.* In the case of α , there is no such perfect screening: the exchange integral is small because each of the charges involved is separately small.

[In this analysis it has been tacitly assumed that the wave functions are positive everywhere, or at least in the region of important overlapping. This will be true of bonding orbits. With non-bonding orbits, where nodes occur in the region of overlapping, the factor s may be exceptionally small, or zero, due to cancellation of positive and negative contributions, and will not serve as a basis of reference for orders of magnitude.]

We now examine the case of three electrons in three orbits. Upon separating off the unperturbed energy, we obtain the complete expression for the interaction energy in a form identical with that given by Slater for the total energy:

$$\begin{aligned}\epsilon &= (N + 2\sqrt{M})/D, \\ N &= P(p - q - r) + Q(q - r - p) + R(r - p - q), \\ M &= P^2qr + Q^2rp + R^2pq + PQ(r - p - q)r \\ &\quad + QR(p - q - r)p + RP(q - r - p)q, \\ D &= p^2 + q^2 + r^2 - 2pq - 2qr - 2rp, \\ P &= C - a + \alpha - \beta/2 - \gamma/2, \\ Q &= C - a + \beta - \gamma/2 - \alpha/2, \\ R &= C - a + \gamma - \alpha/2 - \beta/2, \\ p &= 1 - \pi\kappa\rho + \pi^2 - \kappa^2/2 - \rho^2/2, \\ q &= 1 - \pi\kappa\rho + \kappa^2 - \rho^2/2 - \pi^2/2, \\ r &= 1 - \pi\kappa\rho + \rho^2 - \pi^2/2 - \kappa^2/2.\end{aligned}\tag{8}$$

P , Q , R , and p , q , r , respectively, are the diagonal matrix elements of H' and of 1 over the three wave functions which correspond to electron-pair bonds between atoms $B-C$, $C-A$, and $A-B$, respectively. (We have interchanged Slater's assignments of Q and R in order to get a symmetrical permutation scheme.)

$$\begin{aligned}\pi &= \int bcdV, \quad \kappa = \int cadV, \quad \rho = \int abdV, \\ C &= (abc/H'/abc) = (A - aa)/(B - bb) \\ &\quad + (B - bb)/(C - cc) + (C - cc)/(A - aa), \\ 2a &= (abc/H'/bca) + (abc/H'/cab) \\ &= \kappa(\rho A - ab)/(\pi B - bc) + \rho(\pi B - bc)/(\kappa C - ca) \\ &\quad + \pi(\kappa C - ca)/(\rho A - ab) + \rho(\kappa A - ac)/(\pi C - cb) \\ &\quad + \pi(\rho B - ba)/(\kappa A - ac) + \kappa(\pi C - cb)/(\rho B - ba), \\ \alpha &= (abc/H'/acb) = \alpha_2 + \alpha_3, \\ \beta &= (bca/H'/bac) = \beta_2 + \beta_3, \\ \gamma &= (cab/H'/cba) = \gamma_2 + \gamma_3, \\ \alpha_2 &= (\pi B - bc)/(\pi C - bc); \\ \alpha_3 &= \pi[(A - aa)/(\pi B + \pi C - 2bc)].\end{aligned}\tag{9}$$

Insofar as the non-orthogonality integrals π , κ , ρ , may all be regarded as small quantities of the first order, we see that the Coulomb term C is, as before, a subordinate term of the second order, due to self-screening. In fact, it is identically the sum of the three C 's corresponding to the three two-electron problems. The components of the triple-exchange term, a , have the form: small factor times integral very similar to the α term in the two-electron problem (7). The only difference is that the two diffuse charges are not now coincident; they do, however, more or less overlap, since they contain one wave function as a common factor. This term is, then, of the third order. Of the remaining exchange integrals α , β , γ , the parts α_2 , β_2 , γ_2 are identically the exchange terms of the respective two-electron problems. The terms α_3 , β_3 , γ_3 , have the form: small factor times what may be called a semi-Coulomb integral, since it is the mutual energy of a self-screened distribution and two poorly-screened but small distributions. They are, therefore, presumably of the third order. Since both C and α are commonly negative in the two-electron problem, the analysis just completed leads us to expect that all the integrals in the three-electron problem will likewise be negative.

Since P , Q and R contain no terms larger than the second order, we shall make no error of order higher than the fourth if we follow Slater in introducing the approximation $p = q = r = 1$, and this gives just the London formula. (It should be

noticed, however, that Slater was not justified in taking this step before separating off the unperturbed energy; also, that this is not equivalent to assuming the vanishing of the non-orthogonality integrals π , κ , ρ , which must be retained in calculating the separate terms, according to (9).) With three electrons, as with two, the relative accuracy of the London approximation (compared to the strict H.-L. computation) should be of the order of the square of the non-orthogonal integrals. But we can no longer predict the sign of the error, which depends upon the ratios of the various integrals. Thus, if one bond predominates greatly in strength, the problem will naturally approach the simple two-electron problem, and the error will be similar. If two bonds are equivalent, and stronger than the third, as in the problem of three H atoms in a line at equal distances, the formulas become extremely simple. Thus, if atom B is in the center, we have $\pi = \rho > \kappa$, $|\alpha| = |\gamma| > |\beta|$, and hence

$$\epsilon = [Q - 4R]/[q - 4r] \\ = [C - a + \gamma - \beta]/[1 - \kappa\rho^2 + \rho^2 - \kappa^2]. \quad (10)$$

The London formula omits everything after 1 in the denominator. If ρ greatly exceeds κ this will produce the same kind of error as with two electrons; otherwise the error may be much less. If all three bonds are equivalent, we have

$$\epsilon = R/r = [C - a]/[1 - \rho^3]. \quad (11)$$

Here the error caused by omitting ρ^3 is of opposite sign, and of higher order.

This analysis provides formal justification for the London approximation for two and three electrons, and could doubtless be extended to more complex cases. If, however, we wish to go still further and adopt assumption (D) which must be done if we are to put into the London formula integrals which have been calculated for the simple two-electron problems (or taken from diatomic spectra with the aid of assumption (E)) we must further neglect the third-order terms a , α_3 , β_3 , γ_3 . This will lead to more serious errors, especially in the case of the triple-exchange term, which always comes in with the same sign, while the semi-Coulomb terms partly cancel each other.

With regard to assumption (E), little can be

said, since it appears to be completely without theoretical justification. The concepts of Coulomb and exchange terms are inseparable from the point of view which regards binding energy as a small perturbation, incapable of distorting the atomic wave functions. This point of view reaches its perfect expression in the strict H.-L. treatment. As soon as the atomic wave functions are modified in any way in constructing the molecular function the whole treatment breaks down, since we can no longer separate off the atomic energy and work with a perturbation operator, but must compute the whole energy of the system and then subtract the atomic energy from the answer. Even if the modified molecular wave function is of a type which assigns the electrons to orbits associated with the individual nuclei, so that the resulting expression for the whole energy contains some terms in which the electrons remain stationary, while in others they make transitions, there is no unique way of determining from these the C and α of the H.-L. method, since we do not know what fraction of the atomic energy to subtract from each part. If the molecular wave function contains ionic terms, or terms in which each electron is shared by both nuclei (as in the principal terms of the best function which we have found for H_2) the whole discussion is meaningless. Similar statements can be made about the problem of three atoms, and it is wholly gratuitous to assume that the relation between the true energies in the two- and three-body problems is of the form given by the H.-L. treatment for approximations to these energies. All that can be said is that the results of the latter are certainly numerically too small in both cases (provided they are negative in sign), so that any process by which they are increased will improve the results, if not carried too far. The use of exchange integrals numerically larger than those computed, whether derived from spectra or by purely arbitrary increase, is such a process.

It appears, then, that the use of approximations A , C and D , together with empirical or calculated exchange integrals, should give good relative accuracy for widely separated atoms, where the non-orthogonality integrals are actually small. But for calculating equilibrium or activation energies this condition is not well

met, and it becomes important to have actual information concerning the errors introduced by the various assumptions. We have therefore made some computations to illustrate the matter.

2. ILLUSTRATIVE COMPUTATIONS

The first computation refers to three H atoms in a straight line, at equal distances $1.7 a_0$, the

critical configuration in the reaction $H_2 + H = H + H_2$, according to Eyring and Polanyi. The strict H.-L. calculation proceeds according to Eq. (10), with the following computed values, with which are compared the corresponding "empirical" values, as selected by those authors from spectral data. Values are expressed in kg cal. per mol:

Integral	C	a	β_2	β_3	α_2, γ_2	α_3, γ_3	κ	π, ρ
Computed	-25.1	-44.8	-14.7	-8.7	-93.1	+0.5	0.275	0.669
Spectral	-21.5	0	-18.1	0	-87.3	0	0	0

In order to illustrate the effects of the separate classes of terms on the result, we present the energy as computed with several selections of terms, first without, and then with, inclusion of the factor $1 - \kappa\rho^2 + \rho^2 - \kappa^2$ (having the value 1.249) which forms the denominator in (10). (See Table I.) These values represent the total mu-

TABLE I. Values of ϵ , in kg cal. per mol.

Terms included	$-\epsilon$ without factor	$-\epsilon$ with factor
γ_2, β_2	78.4	62.7
γ_2, β_2, C	103.5	82.9
γ_2, β_2, a	33.6	27.0
γ_2, β_2, C, a	58.7	47.0
$\gamma_2, \gamma_3, \beta_2, \beta_3$	69.2	55.4
$\gamma_2, \gamma_3, \beta_2, \beta_3, C$	94.3	75.5
$\gamma_2, \gamma_3, \beta_2, \beta_3, a$	24.5	19.6
$\gamma_2, \gamma_3, \beta_2, \beta_3, C, a$	49.5	39.7
Spectral β_2, γ_2, C	90.1	

tual energy of the three atoms. The quantity of principal interest is the difference between this and the energy of H_2 in its lowest vibrational state (-66 computed, -103 from spectra). This difference is, for the activation configuration, the activation energy. Since the activation configuration would have to be determined separately for each method of approximation our values cannot be interpreted immediately in terms of predicted activation energies.

Assumption (A) gives $\epsilon = -39.7$. Adding assumption C changes this to -49.5 . Inclusion of assumption (D) further depresses the result to -103.5 , and stable H_3 is predicted. The spectral value -90.1 should be compared, not with -103.5 , but rather with -82.9 , since, in estimating the spectral exchange terms, the authors deliberately neglected the factor $1 + s^2$ in hope of compensating partially the error due to neglect-

ing the corresponding factor in the London formula. We have seen that this is reasonable where, as in this case, the two equivalent bonds greatly preponderate over the third. We may compare the result of the strict H.-L. computation, $66 - 39.7 = 26.3$ with the "semi-empirical" value $103 - 90.1 = 12.9$, and, with due caution, with the experimental value of 7.2 for the activation energy. In this case it is clear that the "semi-empirical" method neglects terms which are separately much larger than the quantity sought; its success is due to extensive cancellation of the errors.

The computation of triple-exchange and semi-Coulomb integrals is exceedingly laborious in the present state of the art, and we have not undertaken the calculation of other examples expressly for the purposes of this article. It is instructive, however, to make use of certain material in the previous computation on H_2O , which, though not corresponding to any actual three-electron problem, will be typical of certain such cases.

We first consider that A and C are hydrogen atoms in the normal state, and B a fictitious atom having all electrons negligible except for a single electron in a 2-quantum s orbit like that of an oxygen atom. The distances $B-A$, $B-C$ are each $2 a_0$, and lie at right angles, so that the $A-C$ bond is now not greatly weaker than the others. Eq. (10) applies as before. In the second example, the B atom shall consist essentially of a $2p$ electron of the Slater-Pauling type, the axis directed towards the A atom. The symmetry is now destroyed and we must go back to Eq. (6). Moreover, one of the non-orthogonal integrals is now identically zero, because of the node in the p orbit.

The required quantities are

Integral	C	a	α_2	α_3	β_2	β_3	γ_2	γ_3	π	κ	ρ
s -orbit	-28.3	-31.2	-49.3	-6.2	-30.8	-7.5	-49.3	-6.2	0.456	0.384	0.456
p -orbit	-40.4	+ 5.2	+13.7	0.0	-30.8	-9.7	-15.8	-0.4	0.000	0.384	0.328

and the result of the calculation is

Approximations	B	B and C	B , C and D
s -orbit	-14.6	-14.3	-46.8
p -orbit	-82.0	-92.5	-79.5

The success of approximation C in the case of the s -orbit is due to the fact that the factor which it neglects, $1 - \kappa\rho^2 + \rho^2 - \kappa^2$, is here 0.981, or practically unity, because of the approximate equality of all three bond strengths.

3. STATUS OF THE "SEMI-EMPIRICAL" METHOD

Our results indicate that in treating 3-electron systems the approximations usually applied in the computation of activation energies involve the neglect of terms of very considerable importance. The results of such computations cannot, therefore, be considered as *bona fide* predictions of quantum mechanics. The further extension of the ideas arising from these simplified computations to the treatment of more complicated systems is also noted to be without theoretical justification. It follows that the relation of quantum mechanics to the so-called "semi-empirical" method is merely suggestive, rather than justificatory.

There can of course be no logical objection to the application of this method as a purely empirical one; as such its justification can arise from its effectiveness in dealing with a large

number of special problems. From this point of view it has in fact attained a very remarkable degree of success. It is indeed surprising that in a fairly large number of cases a reasonable degree of accuracy has been obtained through what is, from a theoretical point of view, the cancellation of a number of serious and apparently unrelated approximations. We have noted how several of these tend to counteract each other, but quantitative considerations of this cancellation are as yet entirely lacking.

Perhaps the most important use of the "semi-empirical" process lies in its indication as to which of two alternative chemical processes may be responsible for a chemical change. One may reasonably hope that in the computation of the activation energies of two similar reactions the errors due to the approximations may be similar, so that the sign of the difference of the two activation energies will come out correctly, if that quantity is not too small. The way in which this difference depends on certain of the approximations, such as the variable choice of a ratio for the coulomb and exchange integrals, can be ascertained. In the absence of similar tests of the influence of the other approximations the determination of the limits within which confidence in this process is justified must likewise await the accumulation of empirical evidence.