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**The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors**

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A new direct difference method for the computation of molecular interactions has been based on a bivariational transcorrelated treatment, together with special methods for the balancing of other errors. It appears that these new features can give a strong reduction in the error of the interaction energy, and they seem to be particularly suitable for computations in the important region near the minimum energy.

It has been generally accepted that this problem is dominated by unresolved difficulties and the relation of the new methods to these apparent difficulties is analysed here.

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1. INTRODUCTION

An accurate knowledge of interaction potentials for molecular systems is of fundamental importance to the understanding and prediction of the properties of imperfect gases, liquids and solutions. In principle the interaction potential of two molecules A and B at a distance  $R$  apart can be computed exactly from the definition

$$\Delta_{AB}W(R) \equiv \bar{W}_{AB}(R) - \bar{W}_A - \bar{W}_B, \quad (1)$$

where the total energy of the interacting system  $\bar{W}_{AB}$  and the energies of the two separate molecules  $\bar{W}_A$  and  $\bar{W}_B$  are obtained from solutions of the appropriate Schrödinger equations. The difficulties of these problems are however shown by the fact that it has not yet been found possible to make quantitative predictions of the interaction potential of two  $H_2$  molecules to sufficient accuracy to provide a reasonable basis for quantitative predictions of physical phenomena. The calculation for more complicated small molecules seems to have been universally regarded as hardly foreseeable. However, it is with the aim of making contributions to such possibilities that the present investigations are being made. There are still elements of conjecture about completely successful predictions but the authors consider that with the analysis here and from some results of applications of these methods to a simple model, it appears that the remaining difficulties are only those of normal detailed investigations.

The present aim is that of predictions in the main region of importance for thermodynamic properties. This is where electrostatic, overlap and dispersion forces have the same order of magnitude and in which these are required to an accuracy of  $10^{-5}$  to  $10^{-7}$  atomic units.

The problems for this intermediate range are very different from the range where the molecules are closer and interacting much more strongly. This latter range is not very useful for thermodynamic properties and the type of accuracy so far considered adequate involves errors about  $10^4$  greater than the above desiderata.

The various previous investigations in this repulsive short range give little hope for the solution of the difficulties of the present range. On the other hand, the long-range calculations, where only dispersion forces need be considered, have a very attractive simplicity compared with the present range. Here perturbation methods are adequate but the results have very little to contribute directly for thermodynamic predictions, apart from qualitative guidance, because the methods seem to be ineffective for the intermediate range.

In the present series of papers some procedures will be examined and developed; these give a hope of a complete solution of the quantum ab initio prediction of interaction potentials for molecular systems. It is considered that the desirability of obtaining a predictive accuracy of about 1 per cent in the interaction potential in the region of the minimum exceeds all other problems in the prediction of the interaction potentials. The present approach contains some new features that seem to make it possible for direct calculations with this accuracy even in this region. Although the long-range predictions are not regarded as of first importance, it may be remarked that the relevant new aspects are applicable to them. In a following paper a subtle test which gives an accuracy of  $10^{-12}$  in a direct difference calculation apparently by using only numerical operations to an accuracy of  $10^{-10}$  will be explained.

The whole issue has a number of complications, and for this reason it has been thought best to establish the validity of the general procedure at various levels. In this paper we shall discuss the main theoretical characteristics of this new method and treat a number of particular mathematical aspects. Some new features have been devised to give a high reduction of the errors. Since most of these are new principles, it appeared worthwhile to test their validity in a simplified model before accurate calculation on molecular systems are attempted. The simplified model investigated consists of two hypothetical quantum systems, which each have one electron in one dimension. These results, which will be reported in a subsequent paper, show that the errors are much less than would generally be supposed. An application to a molecular system is also in its early stages.

The outstanding features which will be analysed in this paper are conveniently shown by the titles of the following sections:

2. Bivariational characteristics.
3. The function counterpoise and point counterpoise methods.
4. Direct difference computations of intermolecular energy.
5. Truncation counterpoise characteristics.
6. Relations to perturbation methods.

The recent bivariational theorem [1] has called attention to the fact that there can be very strong reduction in the errors associated with certain kinds of numerical investigations. This does cause the errors in such calculations to be much smaller than the errors in the individual integrals used in the calculations. This is one reason to hope that errors can be much less than might be feared. In § 3 it will be shown that while retaining this aspect it is possible to introduce two other characteristics which reduce the errors further. § 4 deals with the theoretical formulation of the present method. The discussions in §§ 5 and 6 deal with other aspects that are considered to show that the present method provides a hope of accuracy well beyond that generally expected for earlier methods.

Since in the literature there are many cases where operations on functions are discussed before these are made completely antisymmetric, it should be noted that the discussion here will only be concerned with functions which are completely antisymmetric. All stages of the analysis will, in fact, be carried out as if the complete antisymmetry operator was contained in the front of every expansion function.

## 2. BIVARIATIONAL CHARACTERISTICS

Boys [1] has given a bivariational treatment which enables approximations for the eigenvalue  $\bar{W}$  and eigenfunction  $\Psi$  of the Schrödinger equation

$$(H - \bar{W})\Psi = 0 \quad (2)$$

to be computed in certain important practical cases with a greater accuracy than that one could obtain from usual Rayleigh–Ritz variational procedures because more satisfactory expansion functions can be integrated in the new method. When a numerical integration procedure is used to evaluate the secular matrix elements, the bivariational equations can be written in the form

$$\left. \begin{aligned} \langle \Phi_r^\dagger | Q^\Delta (H - W) | \sum_s Y_s \Phi_s \rangle &= 0, \\ \langle \sum_s Y_s^\dagger \Phi_s^\dagger | Q^\Delta (H - W) | \Phi_r \rangle &= 0, \end{aligned} \right\} \quad (3)$$

where the usual quantum notation  $\langle | \rangle$  is used for integration over all continuous variables and summation over all discrete variables. The operator  $Q^\Delta$  is defined for the case of  $3N$  dimensions to have the form

$$Q^\Delta = \sum_i h_i \delta(\mathbf{r}_1, \mathbf{R}_i) \sum_j h_j \delta(\mathbf{r}_2, \mathbf{R}_j) \dots \sum_u h_u \delta(\mathbf{r}_N, \mathbf{R}_u), \quad (4)$$

where  $\mathbf{R}_k$ ,  $h_k$  are a specified finite set of numerical points and weights for integration in three dimensions, and  $\delta$  is the quantum delta function in three dimensions. This operator constitutes a direct approximation to the continuous integration of the matrix elements by a sum of values at a finite number of points. If an infinite set of integration points with appropriate weights is used in (4), the integration procedure could be perfectly accurate, which would mean that  $Q^\Delta = 1$ .

The Boys bivariational theorem provides the interesting information that the error in  $W$ , obtained by solving equations (3) as an approximation to the true eigenvalue  $\bar{W}$ , will be of order  $O(\mu^\dagger + \mu^\Delta)\mu$ . In this formula  $\mu^\dagger$  and  $\mu$  are unknowns which are defined to be the least squares errors in fitting the true adjoint and direct eigenfunctions  $\Psi^\dagger$  and  $\Psi$  of the Hamiltonian  $H$  by linear combinations of the expansion functions  $\Phi_s^\dagger$  and  $\Phi_s$ , respectively.  $\mu^\Delta$  is a measure of the error introduced by the  $Q^\Delta$  numerical integration procedure. For general applications, such an error is not as satisfactory as the corresponding  $\bar{\mu}^2$  error in a variational procedure, where  $\bar{\mu}$  denotes the least squares error in fitting  $\Psi^\dagger = \Psi$  with the same set of expansion functions  $\Phi_s$ .

But in cases where it is possible to use a set of  $\Phi_s$  which gives a  $\mu$  value much smaller than the corresponding  $\bar{\mu}$  given by the best variational set  $\Phi_s$ , the total error  $(\mu^\dagger + \mu^\Delta)\mu$  can be smaller than  $\bar{\mu}^2$ . And this means that in these cases a bivariational procedure provides energy values more accurate than those one could obtain from a

variational procedure. The atomic and molecular computations by Boys and Handy [2] are examples of cases where errors  $(\mu^\dagger + \mu^\Delta)\mu < \bar{\mu}^2$  have been obtained.

The bivariational  $W$  does not necessarily have monotonic convergence to the true eigenvalue  $\bar{W}$ , so that this advantage of the variational method for the lowest eigenvalue has been lost. But the increase of accuracy that can be obtained with a bivariational treatment will probably outweigh this disadvantage in the present practical applications.

It must be noticed that the  $\bar{\mu}^2$  error variational formula implies an exact integration in the variational secular equations. On the other hand, in a bivariational treatment a numerical integration procedure can be used in the solution of the secular equations. The replacement of the exact integration with a  $Q^\Delta$  numerical integration procedure which gives an error of about  $\mu^\Delta$ , introduces an error in the approximate eigenvalue  $W$  of order  $\mu^\Delta\mu$ . And in all the cases where  $\mu$  can be made very small, the numerical integration error  $\mu^\Delta\mu$  becomes much smaller than  $\mu^\Delta$ . This feature suggests that  $Q^\Delta$  numerical integration procedures can be used with a number of integration points which would not give the desired accuracy in intermediate integrals, but which by the bivariational theory gives the desired accuracy for the final result.

It appears worth while to show these important aspects of the bivariational method in a simple and somewhat extreme example. The hypothetical one-dimensional system examined in this example consists of two simple harmonic oscillators A and B, fixed on the  $x$  axis at a distance  $x_{AB}$  apart. This problem can be solved exactly, and we can compare the exact answer with the approximate results obtained when a fantastically crude numerical integration is used. Let  $x_1$  and  $x_2$  be the coordinates of the two electrons. The notation  $x_{1A} = x_1 - A$ ,  $x_{2A} = x_2 - A$ ,  $x_{1B} = x_1 - B$  and  $x_{2B} = x_2 - B$  will be used. The unperturbed Hamiltonian  $H$  corresponds to two non-interacting simple harmonic oscillators

$$H \equiv -\frac{1}{2} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} - x_{1A}^2 - x_{2B}^2 \right) \equiv H_A + H_B \quad (5)$$

and the perturbation  $V$  consists of the other pair interactions

$$V \equiv -\frac{1}{2}(x_{12}^2 - x_{2A}^2 - x_{1B}^2 + x_{AB}^2) \equiv x_{1A}x_{2B}. \quad (6)$$

The first and second-order bivariational perturbation energies, defined as

$$W_B^1 = \langle \Psi^{0\dagger} | Q^\Delta V | \Psi^0 \rangle / \langle \Psi^{0\dagger} | Q^\Delta | \Psi^0 \rangle, \quad (7)$$

$$W_B^2 = \langle \Psi^{0\dagger} | Q^\Delta V | \Psi^1 \rangle / \langle \Psi^{0\dagger} | Q^\Delta | \Psi^0 \rangle, \quad (8)$$

will be predicted where

$$\Psi^{0\dagger} = \sum_s Y_s^{0\dagger} \Phi_s^\dagger$$

is the zero order adjoint perturbation function, and

$$\Psi^0 = \sum_s Y_s^0 \Phi_s$$

$$\Psi^1 = \sum_s Y_s^1 \Phi_s$$

are the zero and first-order direct perturbation functions. The sets of coefficients  $Y_s^{0\dagger}$ ,  $Y_s^0$  and  $Y_s^1$  can be obtained solving the basic bi-perturbation equations

defined as

$$\left. \begin{aligned} \langle \Phi_t^\dagger | Q^\Delta (H - W^\epsilon + \epsilon V) | \sum_s Y_s^\epsilon \Phi_s \rangle &= 0, \\ \langle \sum_s Y_s^{\epsilon\dagger} \Phi_s^\dagger | Q^\Delta (H - W^\epsilon + \epsilon V) | \Phi_t \rangle &= 0, \end{aligned} \right\} \quad (9)$$

where  $\epsilon$  is the perturbation parameter. The operator  $Q^\Delta$  is the numerical operator  $\sum_i \delta(x_1, X_i) \delta(x_2, X_i)$  taken for integration points at  $X_1 = 0.56491$ ,  $X_2 = 0.61814$ ,  $X_3 = 0.999$  with the constant value 1 for all weights. These integration points were the phone numbers of the authors and of the police station, and were chosen as obviously ridiculously inaccurate but as clearly unadjustable. The expansion functions  $\Phi_s^\dagger$  and  $\Phi_s$  used here are the exact solutions of the zero order, first-order and second-order direct perturbation equations. The table contains the bivariational results obtained here, and for comparison the exact values and some quasi-variational values defined by the following equations

$$W_V^1 = \langle \Psi^0 | Q^\Delta V | \Psi^0 \rangle / \langle \Psi^0 | Q^\Delta | \Psi^0 \rangle, \quad (10)$$

$$W_V^1 = \langle \Psi^0 | Q^\Delta V | \Psi^1 \rangle / \langle \Psi^0 | Q^\Delta | \Psi^0 \rangle. \quad (11)$$

The latter might have been thought to be a more logical alternative to the bivariational expressions (7) and (8) if one did not know the bivariational theorem.

	Exact values	Bivariational with numerical integration	Quasi-variational with numerical integration
First-order energy perturbation $W^1$	0	0.000002	0.426711
Second-order energy perturbation $W^2$	-0.125	-0.124919	-0.113787

Table 1. Values by 7-figure computation.

So in spite of this ridiculous choice of the points of integration a perfect accuracy, apart from decimal point round-off, has been obtained. This result does not depend on the choice of  $\Phi_s^\dagger$ : it can easily be checked that the same result occurs for any choice of  $\Phi_s^\dagger$ . It depends on the fact that the expansion functions  $\Phi_s$  can fit exactly the zero to second-order direct true wave functions. Since this means  $\mu = 0$ , the  $(\mu^\dagger + \mu^\Delta)\mu$  errors in the corresponding bivariational energies become zero.

In a practical example it would not be possible to choose the exact expansion functions  $\Phi_s$  (as in this case), but a large set of  $\Phi_s$  would give a small value of  $\mu$  and hence of  $(\mu^\dagger + \mu^\Delta)\mu$ .

These characteristics suggest that a bivariational approach can be particularly appropriate in direct computations of molecular interactions. It can be noted that in a direct computation of molecular interactions even the variational method would not show a monotonic convergence in the interaction energy, so that in this aspect the bivariational method does not have the comparative deficiency mentioned earlier. It does not appear worthwhile to try to assign detailed merit to the various new aspects of the method for the direct computation of molecular interaction which will

be proposed in this communication, but the authors think that the bivariational characteristics can be reasonably regarded as the dominant feature.

The full implications of the bivariational properties may be unfamiliar and difficult to grasp so that it may be repeated here that it is theoretically possible, with relatively few points of numerical integration, to obtain the same final accuracy as if the coulomb and all the other integrals were accurate to  $10^{-6}$ . This would however require the expansion functions to approximate very closely to the true wavefunction. Of course, the latter is not yet possible, but it is thought that there are greater possibilities of high accuracy in such approaches than is easily realized.

### 3. THE POINT COUNTERPOISE AND FUNCTION COUNTERPOISE METHODS

The term 'counterpoise procedure' will be used as a brief description for some methods by which it is hoped to make some errors in the energy calculations for two separate molecules as nearly equal to the corresponding errors in the bimolecular calculation as possible. These errors can then be expected approximatively to cancel when these quantities are differenced in the computation of the interaction energy.

Before the detailed discussion of these new procedures, a simple example may illustrate the counterpoise idea. This example is a calculation of the energy change of a H-like atom when the nuclear charge  $Z$  is changed from 1 to 1.00001. We shall proceed as if ignorant of the exact answer, as if unable to perform integration, and as if  $\Phi_1 = (1+r)^{-3}$ ,  $\Phi_2 = (1+r)^{-4}$  are the best known expansion functions. In order to compute the energy we merely find  $Y_s$  and  $W$  to satisfy the equation

$$(H - W) \sum_s Y_s \Phi_s = 0 \quad (12)$$

at two different values of  $r$ . For  $r = 0.5$  and  $r = 1.7$  we obtain for  $Z = 1$ , a computed energy value  $W = -0.851375$  A.U., that is, in error by  $-0.351$  from the exact value of  $-0.5$  A.U. When  $Z = 1.00001$  the computed energy value is  $W = -0.851357$  A.U. This is in error by about the same amount from the accurate value of  $-0.50001$  A.U. However, the above quantities give the computed value of the energy change as  $\Delta W = -0.000018$  A.U. to be compared with the accurate value of  $0.000010$  A.U. The error in  $\Delta W$  is in fact  $10^{-4}$  of the  $0.351$  error in the computed energy  $W$ . If we had not used the same points in the computations for both  $Z$  values, then the error in the energy change would have been expected to be of the same order of magnitude as the error in the computed energy. The use of the same points in the computations can be considered a primitive example of point counterpoise.

For molecular computations the point counterpoise procedure consists of an artifice by which just the same set of points and weights is used for composite and separate systems. One set of integration points is chosen for the calculation of the energy  $W_{AB}$  of the bimolecule AB, and this set is also used in the two calculations of the energies  $W_A$  and  $W_B$  of the separate molecules A and B. This might be considered a waste of effort because many points will not give appreciable contributions, but the evidence of a subsequent paper is that with this procedure the error in the interaction energy is reduced to  $1/100$  of its value otherwise. The second type of counterpoise procedure proposed here corresponds closely to the preceding and is the function counterpoise. In this procedure, the calculation of the separate energies  $W_A$  and  $W_B$  are performed with the full set of expansion functions used in the calculation of the energy  $W_{AB}$  of the bimolecular system. It

is considered that a deductive justification for this procedure has not yet been made as for the point counterpoise and this will have to be extensively tested on a preliminary simple model. Results already available do in fact appear to justify it. Hence the whole counterpoise proposals consist of proceeding to the calculation of the energy  $W_A$  just as for  $W_{AB}$ , but merely altering the parameters giving the number of electrons and putting all the nuclear charges in molecule B equal to zero. It may be noted that the counterpoise procedure introduces the rather unexpected feature that the energies of the separate molecules  $W_A$  and  $W_B$  are now slightly dependent on the value of the distance  $R$  between them. And this feature from a computational point of view means that the values of the energies  $W_A$  and  $W_B$  must now be computed at each  $R$  value of the total energy  $W_{AB}$  from which they are to be subtracted.

The complete counterpoise procedure requires an increased computational time but it is obvious that the increase is less than  $2T_{AB}$ , where  $T_{AB}$  is the computational time for  $W_{AB}$ . But a less than three times effort is well worth while if it gives the possibility that much more accurate values of intermolecular interactions may be obtained.

#### 4. THE DIRECT DIFFERENCE COMPUTATION OF INTERMOLECULAR ENERGY

The new general principles have now been described and here it will be attempted to show a way in which a practical computation could be planned on these lines. A plan to use the new methods in a transcorrelated calculation of the type introduced by Boys and Handy [2] will be described. In principle the new methods could just as well be used in the well known configurational interaction method but it is thought from detailed considerations that the transcorrelated method will be more effective.

Such a counterpoise bivariational calculation would consist of the evaluation of the interaction energy of two molecules A and B at a distance  $R$  by

$$\Delta_{AB}^C W(R) = W_{AB}(R) - W_A^C(R) - W_B^C(R). \quad (13)$$

The total energy of the two molecules at a distance  $R$  has the separate energies subtracted with the latter computed by the same points and functions as for  $W_{AB}$ . Hence  $W_A^C$  and  $W_B^C$  vary slightly with  $R$  and the superscript  $C$  is added to denote that all the counterpoise procedures have been used.

All the quantities are to be evaluated by the transcorrelated method in which an approximate wavefunction of the form

$$C\Phi = \prod_{i>j} f(\mathbf{r}_i, \mathbf{r}_j) \mathcal{A}(\phi_1, \phi_2 \dots) \quad (14)$$

is used. The correlation functions  $f(\mathbf{r}_i, \mathbf{r}_j)$  are to be included for all pairs of electrons and they multiply a Slater determinant formed from the space-spin orbitals  $\phi_1, \phi_2 \dots$ . There are to be adjustable parameters  $Y_s$  in both the functions  $f(\mathbf{r}_i, \mathbf{r}_j)$  and in the orbitals. If  $Y_s$  is the full set of parameters then the values of these are determined by

$$\left\langle \frac{\partial}{\partial Y_s} (C^{-1}\Phi) | H - W | C\Phi \right\rangle = 0, \quad (15)$$

$$\left\langle \left( \frac{\partial}{\partial d_s} \log C \right) \Phi | C^{-1}HC - CHC^{-1} | \Phi \right\rangle = 0. \quad (16)$$



We can either state that these equations have to be used with a value of  $W$  satisfying

$$(C^{-1}HC - W)\Phi = 0 \quad (17)$$

or stipulate that the  $Y_s$  contain a parameter which merely allows  $C\Phi$  to be multiplied by a constant. Then this latter equation is contained in (15). Hence we shall regard equations (15) and (16) as the full set of transcorrelated bivariational equations. The optimum  $C\Phi$  and the optimum  $W$  can only be obtained when these equations are simultaneously satisfied and the simplest way to obtain this appears to be with an iteration procedure. The  $d_s$  in equation (16) are a special redundant set of parameters which occur in  $f(\mathbf{r}_i, \mathbf{r}_j)$  and which by (16) are so chosen that  $C\Phi$  is uniquely determined in a manner which gives a most gratifying stability to the iteration convergence. Details of the iteration determination of the  $Y_s$  and  $W$  to satisfy (15) and (16) were described for Ne and LiH but there are various possible variants for this stage and probably any approximate generalized Newton-Raphson method can be used for this.

The counterpoise procedures merely require that equations (15) and (16) are used at every value of  $R$  three times, for  $W_{AB}$ ,  $W_A^C$  and  $W_B^C$  with just the same points of integration and the same expansion functions around A and B even when  $W_A^C$  or  $W_B^C$  is being calculated alone.

It will still be a moderately difficult matter to put this method into operation for interesting molecules, and any estimates of the effort necessary for a given accuracy are subjective at this stage. Nevertheless it is probably informative to say that, in transcorrelated computations, errors of 0.1 per cent can be expected in any of  $W_{AB}$ ,  $W_A^C$  and  $W_B^C$  and that the authors hope that, with the counterpoise effects, the error in  $\Delta_{AB}^C W$  will be brought to an order of magnitude of 2 per cent of the interaction energy value. This hope is not at all inconsistent with the results already obtained in a simplified problem where the one-dimensional interaction of two hypothetical quantum systems each with a unit positive nucleus and one electron is being investigated. Of course in this simple model we are able to achieve a much higher accuracy than that we can expect in real problems. But if we examine situations where the errors in the total energy  $W_{AB}$  are about 0.1 per cent, which corresponds approximately to the order of magnitude of the percentage error in the transcorrelated total energy of LiH, an error in the interaction energy of about 2 per cent is in fact obtained. It must be admitted that the extrapolation of the results from this simplified system to a physical problem is a matter of judgement. However, realistic physical systems are to be tested shortly.

##### 5. TRUNCATION COUNTERPOISE CHARACTERISTICS

Here an awkward source of error will be discussed. This is present either in any perturbation calculation, or in any direct difference calculation in which it is attempted to evaluate the integrals by the most frequently used methods. It is the error which arises because there are no exact formulas for three and four-centre integrals except in Gaussian calculations, and because in Gaussian calculations the convergence of orbitals at large distances is very non-uniform.

In the present method the use of numerical quadrature with one specified set of points for different types of cancelling integrals avoids the above type of error, and this avoidance will here be called 'truncation counterpoise'.

The simplest circumstances where this error arises, in the absence of truncation counterpoise, is in methods depending on evaluation of three and four centre

integrals by other means than Gaussian expansions. It appears in the calculation of the total electrostatic interaction between two molecules in terms of the following type

$$\langle \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) | r_{12}^{-1} - r_{2A}^{-1} - r_{1B}^{-1} + r_{AB}^{-1} | \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \rangle. \quad (18)$$

Such a term would have to be evaluated if a quantitative prediction were attempted either in a perturbation calculation where the first-order term corresponds to the electrostatic interaction, or in a direct difference calculation. Formula (18), where  $\phi_a$  and  $\phi_b$  denote orbitals in the molecules A and B, is a symbolic simplification of the totality of the occurring terms. The nuclear electron interaction terms have been written as if only one nucleus occurred in each of A and B, and as if  $1/r_{2A}$  were one unit of a term  $Z_A/r_{2A}$ , which is considered with  $1/r_{12}$  to show the almost exact cancellation which occurs between the four integrals. The complicated sums which occur in the general case can be resolved into components of the type represented by formula [18], where in the general cases the  $\phi_a$  and  $\phi_b$  involve functions on four centres. The worst four centre integral can only be approximated by multiple infinite series; the  $r_{2A}^{-1}$  three-centre integrals are given by much simpler infinite series; and the other two-centre integrals by exact formulas. Hence the infinite series would have to be continued to terms which are of fantastically high order, compared with present practice, to achieve sufficient accuracy for the final nearly cancelled component; or some way of terminating the series would have to be found to make the errors in the simpler integrals correspond to the truncation errors in the complicated terms. But no such scheme has yet been developed.

In the present method, where expressions of type (18) are evaluated by a numerical quadrature, there is immediately a truncation counterpoise effect if the same points for the integration are used for all the cancelling terms.

It may be pointed out that even if analytical truncation were possible, attempts at increasing the accuracy would involve terms of rapidly increasing complexity, which would make a such procedure very unsuitable for practice. On the other hand, in attempts at increasing the accuracy in numerical integration the computational effort increases simply with the number of points.

If the orbitals are expanded in Gaussian functions the above comments do not apply because there are explicit formulas for the basic integrals. But in this case the truncation in the approximation to a real physical orbital by a finite number of Gaussians gives a corresponding effect. We will refer to this effect as a Gaussian truncation and the main circumstances where errors due to a Gaussian truncation arise are in the computations of integrals containing the two-centre product  $\phi_a(\mathbf{r}_i)\phi_b(\mathbf{r}_i)$ . This is the case for overlap integrals, exchange integrals and some of the nuclear attraction three-centre integrals. Any integral containing  $\phi_a(\mathbf{r}_i)\phi_b(\mathbf{r}_i)$  is in fact contributed nearly completely by the Gaussian functions with greatest width. This domination becomes more and more important when the overlap value becomes smaller and smaller. The behaviour as the number of Gaussians is increased in two slightly overlapping orbitals is likely to be extremely oscillatory as larger and larger Gaussians are used to fit the tails of the orbitals. So that at the large internuclear distances corresponding to the intermediate range where the overlap values are very small, the number of Gaussians would have to be increased in an impractical way to keep anything approaching a constant fractional error in this kind of integrals. The behaviour as the intermolecular distance is increased is like some very peculiar series in which the terms behave so that when

the whole sum is getting less and less it is necessary to take more and more terms to keep some specified accuracy.

It might be thought that to some degree a similar characteristic might enter with numerical quadrature. This is not so because it is not difficult to arrange that a given fraction of the points for integration always occurs in the general area of the overlap, even if the molecules are drawn farther and farther apart. A particular example of such a device has already been used many times and will be described in a subsequent paper where the application of the present method to a simplified problem will be discussed.

The Gaussian truncation error is not the same as the preceding series truncation error, but, since both these originate in an omission of the higher terms of a complete set, it does seem convenient to describe both of them as due to a lack of truncation counterpoise. The truncation counterpoise is thus a very gratifying consequence of the numerical quadrature, but it probably might not be sufficiently effective if it were not associated with the bivariational effects too. But in a procedure where the points of integration are chosen as accurately as possible and all steps are taken to make the bivariational procedure as effective as possible it seems reasonable to say that the present method possesses a truncation counterpoise.

## 6. RELATIONS TO PERTURBATION METHODS

In the first place it must be recognized that perturbation theory is a very powerful analytical tool for the interpretation of physical phenomena and for the deduction of inter-relations between different physical properties, but that, apart from the first-order perturbed energy, it does not provide practical computational methods for quantitative predictions. The physical effects examined here, even at their simplest stage, require second-order terms. For any perturbation computation after the first-order term it is necessary to introduce a variational approximation either directly, or in the special form of using finite perturbations and of interpolating back to small perturbations. However, the hopes of applying such perturbation-variational methods to predictions for the intermediate range have not been found possible because there are abnormal complexities in the theoretical formulation which have not been satisfactorily resolved and whose resolution would be necessary before a computational stage could be reached.

The outstanding one of these complexities is concerned with the virtual excited levels of the unperturbed systems which are used in orthodox perturbation theory as an expansion basis. If the excited levels of the separate molecules are multiplied together and antisymmetrized to form such a basis then the higher terms are doubly overcomplete, not orthogonal, and subject to such large perturbations that these can only be called alterations. The problems associated with these complexities have been investigated in a variety of special and erudite analyses. The present situation is summarized in a review by Hirschfelder and Meath [3]. However, it appears to be generally accepted that there is not yet any foreseeable hope of a resolution of these complexities. In addition to these there is the other unsolved difficulty of the near cancellation of different kinds of electrostatic integrals in the first order perturbation energy. Thus the hope of quantitative perturbation investigations is still dominated by the difficulties which will be referred to as the doubly complete basis and the electrostatic near-cancellation. These issues are further obscured by the fact that perturbation methods can provide accurate

predictions of the so called long-range interactions for simple systems, such as those with an atom for a component, where the electrostatic near cancellation does not occur. But these calculations do not in fact affect the problems of the computation of interaction in the region of the energy minimum, because they are restricted to a range where the overlap integrals, which determine the minimum, are zero. Such calculations have their own interest but they are so based on omission of the difficult terms that they seem to provide no contribution to the more complicated problem of the quantitative prediction in the dominant cohesive range. Incidentally such calculations would still have the electrostatic near cancellation difficulty if they were applied to more complicated molecules. As a result of these factors the perturbation methods do not appear to suggest solutions for these dominant difficulties and the various counterpoise devices were developed. Nevertheless the form of the latter can be seen to owe much to the general knowledge of the perturbation theories.

The electrostatic near cancellation difficulty appears in the computation of the first-order perturbation energy of two interacting molecules A and B in the region of intermediate and large separation just as it has been described in § 5 for the variational calculation. The first-order energy can be resolved into a linear combination of components the predominant ones being terms of the type defined by

$$\langle \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) | r_{12}^{-1} - r_{1B}^{-1} - r_{2A}^{-1} + r_{AB}^{-1} | \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \rangle. \quad (19)$$

Such a term represents the interaction of an orbital  $\phi_a$  in molecule A with an orbital  $\phi_b$  in molecule B, the interaction of these orbitals with nuclei in opposite molecules, and the interaction between the nuclei themselves. At intermediate and long range these four contributions are nearly equal and the final result is a second-order small quantity compared with any of the component integrals. Since these second-order small quantities give the main contribution to the first-order energy, they are required to a very high accuracy. But the required accuracy would be completely beyond the possibility of computational methods without truncation counterpoise characteristics. In the method suggested here truncation counterpoise characteristics arise naturally and this source of error is avoided by evaluating the integrals by a point quadrature with the same points for all cancelling terms, even when alternative methods are available for some of the integrals. The use of a unique grid for the point quadrature could also be applied to perturbation calculations. This suggestion does not arise from perturbation concepts or investigations, but it is a contribution of the present truncation counterpoise procedure to the solution of a perturbation problem. Very laborious computation would however still be necessary if this source of error were not also very strongly dominated by the bivariational effect. The latter improves the situation because it introduces an error of  $O(\mu^\dagger\mu + \mu^\Delta\mu)$  which will tend to zero with  $\mu$ , in spite of the possibility of finite errors in the individual integrals.

The formal complexities associated with the double completeness provide one of the most complicated issues in perturbation theory of molecular properties. It is not possible to review these adequately here but some examples of how these cause very puzzling difficulties will be given.

For brevity the case of two molecules A and B with the same number of electrons will be considered. First the natural set of expansion functions would appear to be  $\mathcal{A}\Phi_k^A\Phi_l^B$  where  $\Phi_k^A$  are all the stationary states of molecule A in the absence of B, and  $\Phi_l^B$  are the complementary set for B. But of course these are

much overcomplete because any member  $\Phi_l^B$  can be expanded in terms of the set  $\Phi_k^A$ . Certainly, if the intermolecular separation AB is large, this only arises for high values of  $l+k$ , but this 'interference' value of  $l+k$  becomes lower as AB is decreased. If it is attempted to avoid this by specifying the cut-off values  $l$  and  $k$ , then above some specified value of AB this would give an error which is small, but it would introduce increasing errors as AB is decreased below this value. The ordinary formulas, based on orthogonal functions, for the expansion of all orders of perturbed wavefunctions then become inaccurate.

It may be noted that the long-range calculation of the value  $C$  in a  $-C/r^6$  term does not encounter this difficulty because  $C$  is only obtained as AB tends to infinity and this distance can be made large enough for a cut-off at any desired energy height and thus any degree of smallness of the error can be obtained. This is a matter of taking two limits in the correct order.

It might be thought that the expansion difficulty is a sufficient obstacle but it may be pointed out that the perturbation method is made inappropriate in another way which might persist even if the double completeness were removed. When high excited virtual states of  $\Phi_k^A$ , or any substitute for these which might be used to remove the double completeness, occur in a perturbation expansion then the denominators of form  $(W_l - W_k)$  become altered by large amounts by the introduction of molecule B. They are not at all the relatively unaltered quantities of ordinary perturbation theory. For example we can make a linear combination of the higher states  $\Phi_k^A$  so that this is centred round the position to be occupied by nucleus B. Then, when this nucleus is introduced, an extremely high  $W_l' - W_k'$  can drop to about the level of the lowest excited state of  $\Phi_l^B$ . It is possible to consider this to be a 90 per cent change (or 900 per cent if this is calculated on the new value), and although this is not a diagonal term it does indicate the drastic changes that occur in the matrix of the virtual states.

These are crude illustrations of the matters which have been widely discussed in much more formal arguments in specialist papers on these topics. But whether the view is expressed that second-order perturbation terms are not sufficient, or that this problem is not yet in a suitable form for perturbation, it is generally accepted that there has been no adequate resolution of the problems of computation of the desired quantities. The extensive comparison of calculations based on various procedures of perturbation type for two H atoms by Certain, Hirschfelder, Kołos and Wolniewicz [4] indicates that no agreement can be reached without the inclusion of some contributions of order higher than the second and suggests virtually the preceding conclusions (see also Hirschfelder and Certain [5]).

These difficulties never arise in the present methods. Here the expansion functions are to be chosen with the best care for sake of the composite AB molecule and no further function nearly linearly dependent on these should be introduced. Then exactly the same functions used in the composite AB system are to be used for the component molecules in two separate calculations. This is to be carried to the logical extreme of using the functions chosen to provide a good fit for molecule B even when the calculation is only for molecule A. It is the opinion of the authors that in calculations on the basis proposed here there is no separation of higher-order terms, and that all the effects are included naturally if the procedure can be operated to a sufficient numerical accuracy.

Hence although it is quite clear that the experience of earlier workers on perturbation theory have provided the basic guidance in development of the method

proposed here, these perturbation investigations have perhaps served more as a demonstration of what to avoid than as a basis which has been extended.

## 7. CONCLUSIONS

The outstanding characteristics of the present methods is that they avoid the difficulties frequently cited in the earlier procedures which have been considered for the calculation of the very small interactions between saturated molecules. These new methods have not yet been tested on a calculation corresponding to an actual physical system, so that it can only be conjectured whether they will be sufficiently accurate. However, they contain possible answers to all the difficulties of the well-known methods which are usually discussed. The methods proposed here may be sufficient to obtain the final required accuracy, or it may be that even more effective methods can be developed from them. But they do suggest that any assumption that no direct practical computations can be made in the near foreseeable future is unjustified.

The methods have been put forward as some first contribution towards calculations of the intermolecular forces in the region of dominant physical interest. This is the region where it is necessary to include coulomb, overlap and dispersion forces, although these are not separated in the present method. The final aim which is hoped to achieve is to predict such interaction potential to an accuracy of 1 per cent or so, but it is not possible to say at this stage how much further development will be necessary to achieve this.

Even with these new methods the whole problem is quite formidable and at the present time it is considered most effective to test the improved accuracy on a two-dimensional model for two one-dimensional electrons on two separate nuclei. Although this is not yet completed it may be said that the counterpoise effects have been found to reduce the errors to about 1/100 of the values they would have otherwise. For this model it is possible to use sufficient points in the integration and sufficient expansion functions to obtain virtually exact results. These serve for assessments of the errors found in computations which correspond to degrees of accuracy attainable for molecular systems.

The present situation may be summarized by saying that

1. The bivariational theory shows that there is a much greater potential accuracy to be achieved in direct numerical integration than might otherwise be thought.
2. The calculation of the energy of the separate molecules as if they were just a sub-case of the composite system of two molecules appears to introduce a strong effect of error cancellation. It is the different aspects of this type of effect which constitute the various counterpoise procedures which have been discussed here.
3. The present formulation does not so much solve the various difficulties which have hitherto been regarded as obstacles, so much as arrange that they do not occur in explicit form.

The whole problem is still a question of degree, whether sufficient accuracy can be obtained for reliable prediction of bulk properties but the situation seems to be sufficiently improved by the preceding considerations that it is very desirable to find out what degree of accuracy can be achieved in practice.

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