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Range Relaxation

I. Calculation of Ground State Energy Curves

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The first of three integral forms of the quantum mechanical variational principle is described and a method introduced for the simultaneous optimisation of the whole of a molecular energy curve, or surface, generated for some adiabatic change. Dimensionless parameters in the wavefunction are expressed as functions of the coordinates and the integral of the energy over the whole surface is minimised with respect to variations in these functions. An integral form of the Virial Theorem is proposed as a test that the wavefunction is in scale for the whole range. A preliminary application is made to the H_2^+, H_2 and He_2 systems.

Die erste von drei integralen Formen des quantenmechanischen Variationsprinzips wird beschrieben, wobei eine Methode mit adiabatischen Änderungen zur gleichzeitigen Optimierung der gesamten molekularen Energiekurve (-fläche) eingeführt wird. Dimensionslose Parameter in der Wellengleichung werden als Funktionen der Koordinaten ausgedrückt und das Energieintegral über die gesamte Fläche wird durch Variation dieser Funktionen minimisiert. Zur Überprüfung einer derartigen Wellenfunktion wird eine integrale Form des Virial-Theorems benutzt. Die Methode wird an den Systemen H_2^+, H_2 und He_2 getestet.

Description de la première de trois formes intégrales du principe variationnel de la mécanique quantique et introduction d'une méthode pour l'optimisation simultanée de toute une courbe (ou surface) d'énergie moléculaire engendrée par une variation adiabatique. Les paramètres sans dimension dans la fonction d'onde sont exprimés en fonction des coordonnées et l'intégrale de l'énergie sur toute la surface est minimisée par rapport aux variations de ces fonctions. Une forme intégrale du théorème du viriel est proposée comme test du bon ordre de grandeur de la fonction d'onde dans tout le domaine. Une application préliminaire est réalisée sur les systèmes H_2^+, H_2 et He_2.

Introduction

This paper is concerned with the calculation of the wavefunction for a molecular system undergoing some adiabatic change. The Hamiltonian for the system $H(X)$ is defined by a set of coordinates, collectively denoted X, which characterise the change. For example in the calculation of the potential curve for a diatomic molecule X might be the internuclear distance, or for a calculation of atomic polarisability it would be the field strength.

An approximation $\Psi(X, \alpha_1, \alpha_2, \ldots, \alpha_n)$ to the many electron wavefunction of a molecule can be written down as a function of the varying coordinates X and an arbitrary number of dimensionless parameters α_i, using the well established techniques of quantum mechanics. Given the functional form Ψ the optimal ground state wavefunction for fixed coordinates X is that for which the expectation value of the energy is minimal with respect to the variations in the parameters α_i.

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For some infinitesimal adiabatic change in the coordinates X the functional form Ψ for the wavefunction in any particular approximation may be regarded as remaining the same, while the values of the parameters α_i (defined as optimal), change infinitesimally.

Over any finite range of coordinates X_1 to X_2 the set of parameters α_i thus define a set of functions $\beta_i(X)$. These are continuous functions. They will be termed here "Range Relaxation Functions", and specify the way in which the wavefunction changes with the changing coordinates. The wave function for the whole range of coordinates may be written in terms of these relaxation functions:

$$\Psi(X) = \Psi(\beta_1(X), \beta_2(X), \ldots, \beta_n(X)) . \tag{1}$$

The approach developed here depends on the following theorem which holds for the lowest state of any given symmetry:

The optimal wavefunction of a specific functional form Ψ for a system undergoing an adiabatic change over a fixed range of coordinates X_1 to X_2 is that for which the integral:

$$\int_{X_1}^{X_2} Q(E(X))\, F(X)\, dX \tag{2}$$

is stationary and minimised with respect to variation in the form of the Range relaxation functions $\beta_i(X)$ relating the adjustable parameters in the wavefunction to the coordinates. Here $E(X)$ is the energy of the system for a coordinate value X:

$$E(X) = \frac{\int \Psi(\beta_i(X))\, H(X)\, \Psi(\beta_i(X))\, d\tau}{\int \Psi(\beta_i(X))\, \Psi(\beta_i(X))\, d\tau}$$

and $Q(E(X))$, $F(X)$ are arbitrary, finite, single-valued functions subject to the constraints:

$$\left.\begin{array}{c} \mathrm{Sign}(Q(E)) = \mathrm{Sign}(E) \\ dQ/dE > 0 \\ F(X) > 0 \end{array}\right\} X_2 \geqq X \geqq X_1 .$$

The optimal relaxation functions $\beta_i(X)$ are independent of the functions Q and F. The value of the integral [Eq. (2)] can never fall below that for the true wavefunction with given functions Q and F.

The truth of the theorem can be ascertained from the following arguments, or proved formally using the calculus of variations [12]. Suppose $\beta(X)$ is defined at each individual point X_k within the range over which the integral is defined such that $E(X_k)$ is a minimum. Then it is clear that $\int E(X)\, dX$ is also a minimum. Conversly the minimum of this integral defines a function $\beta(X)$ such that $dE(X_k)/d\beta(X_k) = 0$ at each point. The two auxilliary conditions on $Q(E)$ require that this function decreases as E decreases; and thus at each point both functions have a minimum for the same value of $\beta(X_k)$. The same function $\beta(X)$ is defined by the minima of both the integrals $\int Q(E(X))\, dX$ and $\int E(X)\, dX$. At each point $F(X_k)$ is a positive number and thus the minimum of $E(X_k)\, F(X_k)$ is fixed by the same value of $\beta(X_k)$ as is the minimum of $E(X_k)$. This establishes that there is a function $\beta(X)$ which minimises the integral Eq. (2), and that it is independent of the functions Q and F, given that the auxilliary conditions hold. Furthermore $\beta(X)$ defines the value of the parameter in the wavefunction for which the energy is optimised at each point.

The theorem can readily be generalised to cover a system with n independent coordinates $X^{(k)}$.

For the rest of this paper the only cases considered are those for which $Q(E)=E$. Applications using the full integral are currently under study.

The proof of this theorem in terms of the variational theorem is trivial though its consequences do not seem to have been followed up. Thus within the computational framework of any theory of electronic structure (for example the valence bond theory), we assume a form for the functions β_i depending on one or more adjustable constants. Minimising the integral of the energy over the coordinate range allows one to survey and optimise the whole of an energy curve or surface at a single calculation.

The success of the treatment in predicting experimental results depends on the complexity and flexibility of the functions Ψ and β_i and in practice will represent a balance between the labour expended and the accuracy desired. The choice of satisfactory forms for the range relaxation functions is simplified by the knowledge that not only they are often monotonic but that they may also have well defined limits. For the potential curve of a diatomic molecule for example these could be the united and separated atoms.

The Range relaxation function approach can also be used in making perturbation theory calculations; for example where there is a zero order problem for which the relaxation functions are known.

In this paper an attempt is made to set up the first part of a practical and completely non-empirical computational scheme for this variational approach, and to apply it to the potential curves for the ground states of the H_2^+, H_2 molecules and to the interaction of two ground state helium atoms over a range of internuclear distances 1 to 3 atomic units. The next two papers introduce two further theorems governing variationally optimised "relaxation" functions, and prepare the way for the first serious applications. The simple calculations which follow here have been made to gain experience with the numerical techniques. We confine consideration for the moment to the use of a constant damping function $F(X)=1$.

Evaluation of the Energy Integral

For the potential curve of a diatomic molecule the coordinate varying in the Hamiltonian is the internuclear distance R. The wavefunctions in the following preliminary calculations are of a simple LCAO molecular orbital form, and the adjustable parameters α_i are the orbital exponents. We are faced with the choice of the functional form $\alpha_i(R)$. Clearly the choice becomes less critical the smaller the range to be considered becomes. If no more than the gradient of the surface at some point is desired a linear approximation would suffice. By a more careful choice of the functional form we can make economical use of a small number of adjustable parameters and of the atomic limits to represent the wavefunction over as wide as possible a working range of coordinates. The problem loosely stated is a familiar one in numerical analysis: choose a function which varies in the same way as the one under investigation and incorporate adjustable parameters to take up the difference. Musulin [1] originally suggested a relationship empirically correlating the screening constant with the internuclear distance of the form:

$$\begin{aligned}\alpha(R) &= \alpha(s) + \Delta\alpha \exp(-cR)\\ \Delta\alpha &= \alpha(u) - \alpha(s)\end{aligned} \tag{3}$$

where c is a positive constant, $\alpha(R)$ the orbital exponent at internuclear distance R, $\alpha(s)$ is the separated atom orbital exponent and $\alpha(u)$ that for the united atom to which the molecule reduces at $R=0$. Calculations have been made using this expression since it is so simple and passes to the correct limits. There is no clear means of roughly predicting c *a priori*. Comparative calculations have also been made using the function:

$$\alpha(R) = \alpha(s) + \Delta\alpha\, \varrho(\alpha(s), r > cR)\,. \tag{4}$$

Here r is the distance of a point in space from the nucleus and ϱ the integral of the electron density over all space outside a distance cR for the orbital concerned. This expression was introduced previously by the author. Without any adjustable constant a similar function has been found to give realistic values of the quadratic, cubic, and quartic force constants for a wide variety of diatomic molecules. These molecular parameters depend critically on the scale of the wavefunction and its derivatives at the equilibrium internuclear distance. The derivation of Eq. (4) and its extension to heteronuclear systems, which are largely intuitive, have been given before [2, 3].

Provided the approximate $\alpha(R)$, [Eqs. (3) or (4)], is a reasonably good representation of the optimal relaxation function [an exact solution for the minimum of the integral Eq. (2)], we may expect the energy curve to be close to the limit for one optimised at each point. Such a curve is therefore free from a serious defect inherent in a great many calculated energy curves arising from the use of a fixed basis set which is more appropriate to one atomic configuration than to the rest. The basis for example is often specifically optimised at $R=\infty$. We require a criterion to establish that this is true for the range chosen in any particular calculation. The virial theorem [4] provides this.

For the optimal relaxation function and, provided the basis is fully adjustable for this function alone, the molecular wavefunction obeys the virial theorem at each point in the range:

$$E + T + R(dE/dR) = 0\,. \tag{5}$$

Here E is the total and T the electronic kinetic energy. Eq. (5) leads directly to an integral form:

$$\int_{R_1}^{R_2} T(R)\, dR / (R_1 E(R_1) - R_2 E(R_2)) = 1\,. \tag{6}$$

This ratio has also been calculated and tabulated with each calculation. Any significant departure from the equality of Eq. (6) would imply that the relaxation function was not sufficiently flexible to provide an equally well balanced basis set over the whole of the range used. The energy curve could then be expected to be biassed. The energy is stationary with respect to variations in the optimal relaxation function, and thus a small departure from equality implies no more than a second order inaccuracy in the energy. It should none the less be pointed out that the validity of Eq. (6) for a particular calculation is a necessary, but not a sufficient condition for a successful relaxation function.

The wavefunctions used in these preliminary calculations are quite unsophisticated, though care has been taken to use for them functions which pass to the correct limits as $R \to \infty$ and $R \to 0$. For H_2^+ the simplest LCAO function has been used. For H_2 the Weinbaum function which allows interaction between the two lowest LCAO configurations of ${}^1\Sigma_g^+$ symmetry is used. For He_2 the LCAO function of Huzinaga [6] in which the exponents for bonding and antibonding orbitals are allowed to vary separately was considered adequate.

The range integration step has been performed numerically by Gauss Legendre quadrature. As is well known this is a method of the "highest precision" [7], and with n quadrature points provides exact integration for any function:

$$a + bR + cR^2 + dR^3 + \cdots pR^{2n-1}.$$

In order therefore to make the method as accurate as possible with the smallest number of points we must make sure that the function whose integral we are minimising has negligable values for the higher order coefficients. For the potential curves studied here the nuclear potential has been separated from the integration since it is not particularly suitable for this form of quadrature. In so far as the variation of the electronic wavefunction with change in R can be regarded as the result of a non-uniform linear a scaling operation [2] the principle terms in the energy are covered by an expansion of up to second order. This implies that a ludicrously bare 2-point quadrature could supply a meaningful first approximation. The results at various quadratures indeed bear this out. In other cases the best choice of damping function $F(X)$ may perhaps be the one which allows high precision with a small number of quadrature points.

The numerical integration detracts somewhat from the elegance of the technique, though it should be pointed out that the conceptual framework for an integration and a quadrature of the highest precision allows the number of points to be kept to the very minimum, and ensures at the same time a balanced basis without the tedious necessity for re-minimisation of the orbital exponents at every point. As will be shown in a later paper this does permit relatively rapid calculations of 2 dimensional energy surfaces which would be otherwise inaccessible.

There is a further aspect for which the present extended energy method might be of considerable value in very refined calculations, though it is not followed up further here. Consider the case when the functional form of the wavefunction for a particular value of R depends on a large number of adjustable parameters. Suppose there are several of these which do not affect the energy much and which do not appear to be very likely to alter much with R. It would seem desirable to replace these by constants. If the straightforward procedure of replacing them by the values for one particular value of R were followed this would introduce a very unfortunate bias. If for example the value at the minimum energy were used this would depress the energy at that point more than the others and tend to increase a predicted force constant. On the other hand the present technique would give an optimum for a parameter related to the whole range, without particular bias. This method of fixing the less sensitive parameters by unbiassed constant values might replace a number of otherwise troublesome *ad hoc* estimates.

One final technical point. The 40K machine on which the calculations were performed (Titan) is not equipped with an overlay facility. In order to save core space, and to make rapid and at the same time exact calculation of the many-centre electron repulsion integrals which appear in the energy expression contracted [8] 1*S*-type gaussian expansions [9] of various lengths have been used as a basis more or less closely approximating a Slater basis of orbital exponent 1. The group can be scaled as a whole to make an orbital equivalent to a Slater orbital of arbitrary exponent. The group "orbital exponent" is thus a single number. Although the smaller expansions do not well approximate the Slater *S*-orbital cusps at the nuclei the shape of the energy surfaces seem to be very little affected by the deficiency in the region of interest.

Table 1. *S-orbital expansions in Caussian basis* [a]

No of terms	1		2		3		4	
in expansion	α	Coeff.	α	Coeff.	α	Coeff.	α	Coeff.
	0.28294	1.0	0.201527	0.82123	0.151374	0.64767	0.123317	0.50907
			1.33248	0.27441	0.681277	0.40789	0.453757	0.47449
					4.50038	0.07048	2.01330	0.13424
							13.3615	0.01906
Energy of H atom	−0.424413		−0.485813		−0.496979		−0.499277	

[a] Taken from Ref. [9].

The unscaled expansions used to approximate the 1*S* orbital of hydrogen [9] are shown in Table 1, together with the expectation value of the energy for the atom.

Simple Calculations on H_2^+, H_2 and He_2

In order to gain experience with the numerical techniques a wide variety of calculations were made on the hydrogen molecule ion. Table 2 shows the results of treatments using 2, 4, 6, 8, and 10 Gauss Legendre quadrature points, with gaussian expansions of 1, 2, 3, and 4 terms for the 1*s* orbital. In each calculation the adjustable parameters in the wavefunction were the orbital exponents. Eqs. (3) and (4) were used to give the functional forms for the variation of orbital exponent with change in internuclear distance. The detailed form of this variation was calculated by adjusting the parameter *c* in either of these equations to optimise the energy integral, Eq. (2). The calculated results are practically the same for all quadratures and basis expansions down to the lowest of 2 points and a single gaussian. The differences between the energy integrals for the four alternative gaussian expansions is largely accounted for by the differences in the energy of the hydrogen atom and proton at infinity. Even where the fullest basis is required for the final energy curve much of the labour involved in extensive minimisation could have been avoided using a small quadrature and expansion in a prior calculation[1].

Tables 3 and 4 show the results of further calculations with a variety of quadratures and bases for H_2 and He_2. The encouraging conformity among the results for each molecule is preserved here also.

Between the two alternative forms for the Range relaxation function there seems to be little to choose as far as the energy integral is concerned. Eq. (4) is perhaps to be preferred however in the extension of the method to more complicated systems, since the adjustable parameter comes out as expected, quite close to 1. Considering the relatively large range of 2 a.u. over which the calculations were performed the agreement with the integrated virial theorem, Eq. (6) is quite satisfactory.

Table 2. H_2^+. *Calculations of the electronic energy integral for the* LCAO-MO *function, range relaxation parameter and integral virial ratio using Gauss Legendre quadratures of 2, 4, 6, 8 and 10 points, with gaussian orbital expansions of 1, 2, 3, and 4 terms. The relaxation functions are given by Eqs. (3) and (4).* $\alpha(s) = 1$. $\alpha(u) = 2$. *The range of integration is 1 to 3 a.u.*

Quadrature points	Relaxation function Eq. (3) Number of terms in gaussian expansion of orbital				Relaxation function Eq. (4) Number of terms in gaussian expansion of orbital			
	1	2	3	4	1	2	3	4
2	−2.10411	−2.20832	−2.22255	−2.22567	−2.10458	−2.20526	−2.22099	−2.22409
	0.698	0.726	0.710	0.679	1.058	1.082	1.071	1.074
	0.9960	0.9890	0.9983	1.0218	0.9844	0.9794	0.9886	0.9774
4	−2.10437	−2.20782	−2.22397	−2.22638	−2.10460	−2.20629	−2.22196	−2.22418
	0.700	0.718	0.715	0.710	1.050	1.072	1.063	1.060
	0.9965	0.9874	1.0016	0.9995	0.9909	0.9890	0.9880	0.9880
6	−2.10445	−2.20822	−2.22359	−2.22624	−2.10468	−2.20590	−2.22177	−2.22440
	0.701	0.721	0.713	0.710	1.051	1.070	1.062	1.049
	0.9964	0.9954	0.9972	0.9984	0.9910	0.9901	0.9880	0.9961
8	−2.10448	−2.20833	−2.22356	−2.22650	−2.10471	−2.20618	−2.22209	−2.22426
	0.701	0.708	0.712	0.712	1.051	1.072	1.065	1.060
	0.9964	1.0063	0.9973	0.9950	0.9907	0.9890	0.9870	0.9880
10	−2.10450	−2.20806	−2.22384	−2.22635	−2.10473	−2.20605	−2.22192	−2.22421
	0.701	0.720	0.714	0.710	1.051	1.071	1.062	1.032
	0.9964	0.9954	0.9966	0.9984	0.9905	0.9885	0.9883	0.9833

Phillipson [10] has tabulated accurately optimised parameters and energies for the Huzinaga wavefunction for He_2, at a variety of internuclear distances

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[1] The slight scatter in the results is almost entirely accounted for in the minimising procedure which located the minimum to within about 0.003 units and in approximating the incomplete gamma function by the limiting expression $\int_0^1 \exp(-tu^2)\,du = \sqrt{\pi}/2t^{\frac{1}{2}}$ for values of $t > 3.5$. In later calculations on H_2 and He_2 the range for which the series expansion was used was extended to $t = 5$ and the accuracy of the minimisation procedure reduced to about 0.05.

Table 3. *Range relaxation treatments of* H_2. *Weinbaum function,* $\alpha(s) = 1$. $\alpha(u) = 1.6875$ *electronic energy integral, relaxation parameter and virial ratio in order for each calculation. Range of integration 1 to 3 a.u.*

Quadrature points	Terms	Relaxation function Eq. (3)	Relaxation function Eq. (4)
2	1	−3.01935 0.980 1.0127	−3.02099 1.327 1.0033
2	4	−3.30836 0.943 1.0060	−3.30903 1.296 0.9896
4	2	−3.25510 0.977 1.0082	−3.25588 1.326 0.9949
10	1	−3.01905 0.988 1.0113	−3.02082 1.338 1.0019
10	4	−3.30957 0.933 1.0117	−3.30970 1.299 0.9919

between 0.5 and 2 Å. The repulsive potential is compared in Table 5 with the results of a range relaxation treatment over the same range. The basis is Huzinaga's 4-term gaussian orbital expansion, and is therefore close to, though not the same as that used by Phillipson (the energy of the hydrogen atom being 0.0007 a.u., inferior). The two point quadrature used on the other hand represents the crudest level of range integral optimisation possible. Furthermore the range of the calculation is extremely large, about 3 a.u. These might therefore be expected to represent the worst conditions under which the treatment might be applied. The results shown in Table 5, using Eq. (4) for the relaxation function are really quite close to those of the accurately optimised function, except at very short distances; and represent a substantial reduction in labour. That the basis is not well in scale, and that the range is indeed excessive is shown by the poor value of the virial ratio: 1.2310. The potential is within 1 kcal of the experimental value in the region of greatest "chemical" interest, that is where it lies between 0 and 12 kcal.

Table 4. *Range relaxation treatments of* $He_2\,1\Sigma g_+$. $\alpha(s) = 1.6875$, $\alpha(u_1) = 3.6848$, $\alpha(u_2) = 0.478$[a]. *Electronic energy integral, relaxation parameter and ratio. Range of integration 1 to 3 a.u.*

Quadrature points	Terms	Relaxation function Eq. (3)	Relaxation function Eq. (4)
4	2	−14.86569 1.631 1.215 0.9965	−14.87475 1.136 0.889 0.9897

[a] The united atom orbital exponent 0.9560 given by Clementi *et al.*, Ref. [11] was approximately corrected for the change in principle quantum number by division by 2. The results are quite insensitive to the precise value chosen. Phillipson, Ref. [10] quotes a value of 0.36.

Table 5. *Comparison of the repulsive potential for* He_2 *calculated from the Phillipson-Huzinaga function and from the related range relaxation treatment. The long range (~3 a.u.) and bare quadrature (2 points) exemplify the least favorable conditions under which the treatment might be applied. The 4-term gaussian expansion was used for the basis set, the optimal relaxation parameters are 1.043 and 0.833, and the integral virial ratio is 1.2310 showing that the treatment is over a too extended range*

R (a.u.)	Orbital exponents				Repulsive potential	
	α_g		α_u			
	R.R.	Phillipson	R.R.	Phillipson	R.R.	Phillipson
0.945180	2.39	2.23	1.08	0.99	1.09488	1.05176
1.181474	2.12	2.04	1.26	1.22	0.67286	0.66279
1.417769	1.94	1.92	1.40	1.38	0.41616	0.43379
1.654064	1.83	1.84	1.50	1.49	0.25401	0.25507
1.890360	1.76	1.79	1.57	1.57	0.15386	0.15549
2.126654	1.73	1.75	1.61	1.62	0.09351	0.09379
2.362949	1.71	1.73	1.64	1.65	0.05558	0.05589
2.599244	1.70	1.71	1.66	1.67	0.03217	0.03289
2.835538	1.69	1.70	1.67	1.68	0.01772	0.01908
3.071834	1.69	1.69	1.68	1.69	0.01019	0.01089
3.308129	1.689	1.687	1.682	1.693	0.00583	0.00610
3.544423	1.688	1.684	1.684	1.695	0.00310	0.00334
3.780718	1.688	1.683	1.686	1.695	0.00173	0.00180
∞	1.6875[a]	1.6875	1.6875[a]	1.6875	0.0	0.0

[a] The optimum for the gaussian function is actually about 0.0008 less though the Slater orbital exponent was used for self-consistency.

Conclusions

While it is clearly too early to make any detailed conclusions about this method of calculation the results so far obtained are most encouraging, since they indicate that even with the crudest bases and quadratures meaningful energy curves can be obtained, at a completely non-empirical level. The significance of these crude results is clearly of the greatest importance in extending the method to many-dimensional, poly-electronic systems.

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