Theoret. chim. Acta (Berl.) 1, 36—41 (1962)

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The Use of Interparticle Coordinates in Electronic Energy Calculations for Atoms and Molecules

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The use of interparticle coordinates in atomic and molecular calculations is reviewed and emphasized. For states where the wave function is dependent only upon interparticle coordinates the Hamiltonian is a relatively simple expression. If the wave function is a linear combination of products of functions of single interparticle coordinates of the exponential power form the formulas for local energy are particularly simple.

Es wird über Teilchenabstände als Koordinaten in Atom- und Molekülproblemen referiert und auf ihren Wert hingewiesen. In Fällen, wo die Wellenfunktion nur von Teilchenabständen abhängt, wird der Hamilton-Operator verhältnismäßig einfach. Ist die Wellenfunktion eine Linearkombination von Produkten von Potenz-Exponential-Funktionen einzelner Teilchenabstände, so werden die Ausdrücke für die lokale Energie besonders einfach.

L'auteur fait une revue et souligne l'importance de l'emploi des distances relatives des particules comme coordonnées pour les calculs atomiques et moléculaires. Pour des états dont les fonctions d'onde ne dépendent que de ces distances le l'Hamiltonien devient relativement simple. Si la fonction d'onde s'écrit comme une combinaison linéaire de produits de fonctions exponentielles (à puissances) ne dépendant que d'une seule coordonnée interparticulaire, les formules pour l'énergie locale se simplifient particulièrement.

Introduction

Interparticle coordinates are the magnitudes of the distances between each pair of particles in an atomic or molecular system. These include internuclear distances, electron-nuclear distances, and interelectronic distances. Such coordinates are natural and are attractive from a physical standpoint for a system of several particles. For two-electron systems they have been involved in the most accurate calculations such as those recently published by KOLOS and ROOTHAAN [*7*a, b] for H_2 and PEKERIS [*11*] for *He.*

To be sure, linear combinations of interparticle coordinates, elliptical and perimetric coordinates, respectively, were actually used in these calculations. The advantage of such combinations is to eliminate the dependence between the ranges of the interparticle coordinates. However, for more complex systems such as the *Li* atom or a triatomic molecule no similar combinations seem to be known.

Interparticle coordinates have been used directly in energy calculations for systems of three particles with coulomb interaction and all in relative motion [*8*, *3*].

Interelectronic distances have long been discussed as an aid to introduce electron correlation in wave functions. The use of a correlation factor as in the method of correlated orbitals shows great promise [*7*a, *6*, *4*, *2*, *9*]. Interelectronic distances in the wave function cause grave difficulties in evaluating the integrals needed in the variation method but progress is currently being made in such integrations [*13*, *10*].

Although functions of interparticle coordinates are difficult to integrate it is a simple matter to evaluate the local energy $\boldsymbol{H}\psi/\psi$ and to test the accuracy of the wave function [*1*] or to use this device as a means of improving the function [*5*].

It is the purpose of this paper to discuss the Hamiltonian operator in interparticle coordinates and to display the simplicity and generality of formulas for $\boldsymbol{H}\psi$ and $\boldsymbol{H}\psi/\psi$ for a particular form of ψ.

Coordinates

Consider a system of n particles which may include electrons or nuclei or other charged particles such as positrons or mesons which may enter into atom or molecule formation. The total number of interparticle coordinates is equal to the number of pairs of particles $n(n-1)/2$. The coordinates will be designated r_{ij}, usually with $i < j$. Occasionally to gain simplicity of formulas i may be greater than j but it is only necessary to remember that $r_{ij} = r_{ji}$ and either form may be used.

For more than four particles the number of interparticle coordinates is greater than the number of independent internal coordinates which is $3n-6$. The possible dependence of coordinates will be taken into account in what follows. Since internal coordinates are being used the discussion will apply only to non-translating, non-rotating atoms or molecules. The translation is no problem since it can always be separated off. However the restriction to rotationless systems is serious in as much as only S states of atoms or Σ states of linear molecules can be treated. In principle rotation could be handled by introducing fictitious particles as near neighbors of others, say nuclei, and using a limiting process to generate angular coordinates.

It will be considered at first that all coordinates, including internuclear, are variable. If one wishes to consider a molecule with the usual approximation of fixed internuclear distances it is a simple matter to drop terms in this variable, or what is equivalent, to arbitrarily let the corresponding nuclear masses become infinite.

The Kinetic Energy Operator $\boldsymbol{T}$

In general for a non-relativistic system in atomic units

$$\boldsymbol{T} \equiv -\frac{1}{2}\sum_i \frac{1}{m_i}\nabla_i^2 \tag{1}$$

where the sum is over all particles and ∇_i^2 is the Laplacian operator for particle i. When applied to a function of interparticle coordinates only, ∇_i takes the form

$$\nabla_i \equiv \sum_{j\neq i} (\nabla_i r_{ij}) \frac{\partial}{\partial r_{ij}} \tag{2}$$

and

$$\nabla_i^2 \equiv \sum_{j\neq i}\left(\frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right) + \sum_{\substack{j \\ \neq}} \sum_{\substack{k \\ i}} (\nabla_i r_{ij}) \cdot (\nabla_i r_{ik}) \frac{\partial^2}{\partial r_{ij}\,\partial r_{ik}} \tag{3}$$

In equation (3) the quantity

$$(\nabla_i r_{ij}) \cdot (\nabla_i r_{ik}) = \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{2\, r_{ij} \cdot r_{ik}} = \cos \vartheta_{ij,\, ik} \tag{4}$$

where $\vartheta_{ij,\, ik}$ is the angle at particle i between the radius vectors to particles j and k.

Substituting (4) into (3) and (3) into (1) and removing from the double sum in (3) the terms where $j = k$ and therefore $\cos \vartheta_{ij,\,ij} = 1$ there results

$$T \equiv -\frac{1}{2} \sum_{i<j}\sum \left(\frac{1}{m_i} + \frac{1}{m_j}\right) \left(\frac{\partial_2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}}\right) - \sum_i \frac{1}{m_i} \sum_{\substack{j,\\ j<k}} \sum_{k \neq i} \cos \vartheta_{ij,\,ik} \frac{\partial_2}{\partial r_{ij}\,\partial r_{ik}} \tag{5}$$

The Hamiltonian for a System with Coulomb Forces

The potential energy may be expressed as

$$V = \sum_{i<j}\sum Z_i Z_j / r_{ij}$$

where Z_i is the charge. Therefore the Hamiltonian is

$$H \equiv \sum_{i<j}\sum \left[-\frac{1}{2}\left(\frac{1}{m_i} + \frac{1}{m_j}\right)\left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}}\right) + \frac{Z_i Z_j}{r_{ij}}\right] -$$

$$- \sum_i \frac{1}{m_i} \sum_{\substack{j,\\ j<k}} \sum_{k \neq i} \cos \vartheta_{ij,\,ik} \frac{\partial^2}{\partial r_{ij}\,\partial r_{ik}} \tag{6}$$

This general formula was stated by KOLOS and ROOTHAAN [*7*a] who used it for the particular case of the hydrogen molecule. Although in this case of four particles the six interparticle coordinates are independent (except in their ranges), equation (6) is true in general.

The special case for three particles, in particular the *He* atom, has long been known and used [*6*, *12*]. WALSH and BOROWITZ [*14*] gave the general formula as it applies to any atom with a fixed nucleus.

In the following the system will be restricted to any atom or molecule with fixed nuclei.

The Hamiltonian for an Atom or Molecule with Fixed Nuclei

Equation (6) will apply to this case if m_i for each nucleus is set to infinity and m_i for each electron is unity. Z_i for a nucleus is its atomic number, for an electron —1. It is convenient to distinguish between nuclei and electrons in the indices. Let Greek indices, μ and ν, refer to nuclei and Latin indices, i, j and k, refer to electrons unless otherwise stated. Then (6) can be rewritten as

$$H \equiv \sum_\mu \sum_i \left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r_{\mu i}^2} + \frac{2}{r_{\mu i}} \frac{\partial}{\partial r_{\mu i}}\right) - \frac{Z_\mu}{r_{\mu i}}\right] + \sum_{i<j}\sum \left[-\left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}}\right) + \frac{1}{r_{ij}}\right] -$$

$$- \sum_i \left[\sum_{\mu<\nu}\sum \cos \vartheta_{i\mu,\,i\nu} \frac{\partial^2}{\partial r_{\mu i}\,\partial r_{\nu i}} + \sum_\mu \sum_{j \neq i} \cos \vartheta_{i\mu,\,ij} \frac{\partial^2}{\partial r_{\mu i}\,\partial r_{ij}} + \right.$$

$$\left. + \sum_{\substack{j<k\\ \neq i}}\sum \cos \vartheta_{ij,\,ik} \frac{\partial^2}{\partial r_{ij}\,\partial r_{ik}}\right] + \sum_{\mu<\nu}\sum Z_\mu Z_\nu / r_{\mu\nu} \tag{7}$$

A simplified form of (7) can be obtained by defining the following operators.

Let
$$D_{ij} \equiv \frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial^2}{\partial r_{ij}}$$

and
$$C_{i,\,jk} \equiv \cos \vartheta_{ij,\,ik} \frac{\partial^2}{\partial r_{ij}\,\partial r_{ik}} \tag{8}$$

where one or two of the indices may represent the greek letters in (7). Then (7) becomes

$$H = T + V$$

where

$$\boldsymbol{T} = -\frac{1}{2}\sum_{\mu}\sum_{i}\boldsymbol{D}_{\mu i} - \sum_{i<j}\sum\boldsymbol{D}_{ij} - \\ -\sum_{i}\left[\sum_{\mu<\nu}\sum\boldsymbol{C}_{i,\,\mu\nu} + \sum_{\mu}\sum_{j\neq i}\boldsymbol{C}_{i,\,\mu j} + \sum_{\substack{j<k\\ \neq i}}\sum\boldsymbol{C}_{i,\,jk}\right] \tag{9}$$

and

$$\boldsymbol{V} = -\sum_{\mu}\sum_{i}\frac{Z_{\mu}}{r_{\mu i}} + \sum_{i<j}\sum\frac{1}{r_{ij}} + \sum_{\mu<\nu}\sum\frac{Z_{\mu}Z_{\nu}}{r_{\mu\nu}} \tag{10}$$

In the expression for $\boldsymbol{T}$ there is an operator $\boldsymbol{D}_{\mu i}$ for each nucleus-electron interaction and an operator $\boldsymbol{D}_{ij}$ for each electron-electron interaction. The triple sums, or three-body interactions, in $\boldsymbol{T}$ include, for each electron, a $\boldsymbol{C}_{i,\,\mu\nu}$ operator for interaction with each possible pair of nuclei, a $\boldsymbol{C}_{i,\,\mu j}$ operator for interaction with each possible nucleus-other-electron pair, and a $\boldsymbol{C}_{i,\,jk}$ operator for interaction of electron i with each possible pair of other electrons. For example, for the hydrogen molecule there will be four $\boldsymbol{D}_{\mu i}$ terms, one $\boldsymbol{D}_{ij}$ term, two $\boldsymbol{C}_{i,\,\mu\nu}$ terms, four $\boldsymbol{C}_{i,\,\mu j}$ terms and no $\boldsymbol{C}_{i,\,jk}$ terms. For the lithium atom the various terms number three, three, zero, six and three, respectively.

Because of the possible scaling of the wave function as related to the virial theorem it is useful to keep $\boldsymbol{T}$ and $\boldsymbol{V}$ as separate sums. Of course the last sum in the $\boldsymbol{V}$ expression in (10) which is the internuclear repulsion is independent of the variable coordinates and can be omitted from the Hamiltonian. The energy from the Schrödinger equation would then be the „pure" electronic energy for the system.

Specialization to Linear Combinations of Product Functions

Suppose that a general function, φ, of interparticle coordinates can be expressed as a linear combination of product functions, i.e.,

$$\varphi = \sum_{s} c_s\,\varphi_s \tag{11}$$

where

$$\varphi_s = \prod_{i<j}\varphi_{ij}^{(s)} \tag{12}$$

with $\varphi_{ij}^{(s)}$ a function of r_{ij} alone and a nuclear index may be indicated. Nearly all of the more accurate two and three particle functions are of this form [*7*, *11*, *8*, *3*, *6*, *13*].

In both the variation method and the least square local energy method there is needed the expression for $\boldsymbol{H}\varphi$ which is of course a linear combination of the $\boldsymbol{H}\varphi_s$'s. Because of the product form (12) the local energy expression will be particularly simple.

$$\varepsilon = \boldsymbol{H}\varphi/\varphi = \sum_{s} c_s\boldsymbol{H}\varphi_s/\sum_{s} c_s\,\varphi_s = \sum_{s} c_s\,\varepsilon_s\,\varphi_s/\sum_{s} c_s\,\varphi_s \tag{13}$$

where

$$\varepsilon_s = \boldsymbol{H}\,\varphi_s/\varphi_s \tag{14}$$

Applying (9) to (12) and using (14) the result is

$$\varepsilon_s = -\frac{1}{2}\sum_{\mu}\sum_{i}\frac{\boldsymbol{D}_{\mu i}\,\varphi_{\mu i}^{(s)}}{\varphi_{\mu i}^{(s)}} - \sum_{i<j}\sum\frac{\boldsymbol{D}_{ij}\,\varphi_{ij}^{(s)}}{\varphi_{ij}^{(s)}} - \\ - \sum_{i}\left[\sum_{\mu<\nu}\sum\frac{\boldsymbol{C}_{i,\,\mu\nu}\,\varphi_{\mu i}^{(s)}\,\varphi_{\nu i}^{(s)}}{\varphi_{\mu i}^{(s)}\,\varphi_{\nu i}^{(s)}} + \sum_{\mu}\sum_{j\neq i}\frac{\boldsymbol{C}_{i,\,\mu j}\,\varphi_{\mu i}^{(s)}\,\varphi_{ij}^{(s)}}{\varphi_{\mu i}^{(s)}\,\varphi_{ij}^{(s)}} + \right. \\ \left. + \sum_{\substack{j<k\\ \neq i}}\sum\frac{\boldsymbol{C}_{i,\,jk}\,\varphi_{ij}^{(s)}\,\varphi_{ik}^{(s)}}{\varphi_{ij}^{(s)}\,\varphi_{ik}^{(s)}}\right] + \boldsymbol{V} \tag{15}$$

where now again i, j and k refer only to electrons. The relative simplicity of this equation is realized when it is noticed that each term in the first two sums is a function of a single coordinate while in the triple sums each term is a function of no more than three coordinates.

Specialization to Exponential-Power Functions

Let

$$\varphi_{ij}^{(s)} = r_{ij}{}^{n_{ij}} \exp\left(-\zeta_{ij}\, r_{ij}\right) \tag{16}$$

with a possible nuclear index included as i or j. The power n_{ij} and the value of ζ_{ij} depend in some specifically defined manner upon the index s. Terms in the summations of equation (15) may be expressed with defined functions $A_{ij}^{(s)}$ and $B_{ij}^{(s)}$ as follows

Let

$$A_{ij}^{(s)} = \zeta_{ij}^2 - \frac{2\,(n_{ij}+1)\,\zeta_{ij}}{r_{ij}} + \frac{n_{ij}(n_{ij}+1)}{r_{ij}^2} \tag{17}$$

and

$$B_{ij}^{(s)} = \zeta_{ij} - \frac{n_{ij}}{r_{ij}} \tag{18}$$

then

$$\frac{\boldsymbol{D}_{ij}\,\varphi_{ij}^{(s)}}{\varphi_{ij}^{(s)}} = A_{ij}^{(s)} \tag{19}$$

and

$$\frac{\boldsymbol{C}_{i,jk}\,\varphi_{ij}^{(s)}\,\varphi_{ik}^{(s)}}{\varphi_{ij}^{(s)}\,\varphi_{ik}^{(s)}} = \cos\vartheta_{ij,\,ik}\cdot B_{ij}^{(s)}\,B_{ik}^{(s)} \tag{20}$$

and finally

$$\varepsilon_s = -\frac{1}{2}\sum_{\mu}\sum_{i} A_{\mu i}^{(s)} - \sum_{i<j}\sum A_{ij}^{(s)} - \\ -\sum_{i}\left[\sum_{\mu<\nu}\sum\cos\vartheta_{\mu i,\,\nu i}\cdot B_{\mu i}^{(s)}\,B_{\nu i}^{(s)} + \sum_{\mu}\sum_{j\neq i}\cos\vartheta_{\mu i,\,ij}\cdot B_{\mu i}^{(s)}\,B_{ij}^{(s)} + \right. \\ \left. + \sum_{\substack{j<k\\ \neq i}}\sum\cos\vartheta_{ij,\,ik}\cdot B_{ij}^{(s)}\,B_{ik}^{(s)}\right] + V \tag{21}$$

In order to create matrix components for either the variation method or the least square local energy method one needs the expression for $\boldsymbol{H}\varphi_s$. This is of course just $\varepsilon_s\varphi_s$. The integrand $\varphi_t\boldsymbol{H}\varphi_s$ or the terms to be summed, exclusive of the volume element, are then merely products of single coordinate functions for the „A" and V terms. For the „BB" terms two or three coordinates are intermingled. It is expected that these formulas will be useful for a number of calculations.

Acknowledgement. This research was supported by the National Science Foundation.

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(Note: a factor of one-half is missing from the triple summation in their equation (3.5) since each different term appears twice.)

(Received March 23, 1962)