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1972 J. Phys. A: Gen. Phys. 5 1138

(http://iopscience.iop.org/0022-3689/5/8/007)

J. Phys. A: Gen. Phys., Vol. 5, August 1972. Printed in Great Britain.

Distribution functions in virial and hypervirial theory

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MS received 15 November 1971, in revised form 5 May 1972

Abstract. The forms of the virial and hypervirial theorems are derived when a distribution function, that is, the Laplace transform of a distribution, is taken to define a quantum-mechanical system. The validity of the resulting equations imposes necessary (and sufficient) conditions on the distribution and hence the distribution function. Distribution theory is used to establish the existence of an exponential function satisfying the virial theorem for the Yukawa potential for a restricted range of the defining parameters. For hypervirial relations, the method would seem of little practical importance.

1. Introduction

The idea of considering the wavefunction as the image, under the Laplace transform, of some 'weighting function' has been utilized by Somorjai (1968, 1969), Shillady (1969) and Empedocles (1970). In a computational treatment the parameters used to define the weighting function are optimized variationally, using the minimum of the mean value of the energy as the criterion for the acceptability of an approximate wavefunction. The numerical accuracy achieved by this approach has prompted parallel treatments based on different transform kernels (Billingsley and Shillady 1970, Bishop and Somorjai 1970, Somorjai and Bishop 1970, Yue and Somorjai 1970).

A previous paper (Farmer 1969) argued the case for considering the 'weighting function' as a distribution, in the sense of Schwartz (1966). A treatment, based on the variational principle, was developed and the techniques illustrated by a discussion of the hydrogen-like atom. Whilst other models are amenable to this treatment, impasse is reached if either the helium-like atom or Yukawa potential is considered.

The failure of the theory to provide an analytic solution in these cases motivated the consideration of other criteria which any reasonable variation function should satisfy. In this context Löwdin (1959) has shown that the virial theorem defines a necessary condition on a given system. The virial theorem may be derived as a special case of hypervirial theory and Coulson (1965) has shown that diagonal and off-diagonal hypervirial relations provide necessary and sufficient conditions for the solution of the Schrödinger equation.

The present paper takes the wavefunction defining a quantum-mechanical system, either the exact function or an approximation, as a distribution function, that is, the Laplace transform of some distribution. The forms of the virial and hypervirial theorems appropriate to this definition are derived. The equations from the hypervirial relations, necessary and sufficient conditions for the solution of the Schrödinger equation, will yield exact solutions. In contrast, the virial theory equation, providing only a necessary

condition on the distribution generating the wavefunction, may be used as a criterion to be satisfied in any approximation to an exact specification of the quantum-mechanical system. The analysis of the equations to determine the appropriate distribution, and hence either an exact or approximate wavefunction for the system, is illustrated.

2. Elements of the distribution function approach

For a one-particle system and a spherically symmetric potential, the use of spherical polar coordinates to define configuration space allows the decomposition of the wavefunction Ψ into a radial term R and an angular one Θ given by

$$\Psi(r) = R(r)\Theta(\theta; \phi). \tag{1}$$

In extending the analysis to many-particle systems, such a decomposition of the wavefunction to radial and angular dependence of the form (1) requires that these terms are subject to appropriate symmetry constraints. A first approximation to the wavefunction may be inherent in the assumption of this decomposition.

Another paper (Farmer 1972) shows that, for a radial function R subject to no constraints, the following definition is well made:

$$R(r) = r^{[p]}\boldsymbol{R}^p(r) = r^{[p]}\langle T^p_x, \exp(-x\,.\,r)\rangle = \langle T^p_x, f_p(x)\rangle \equiv \int T^p_x f_p(x)\mu(\mathrm{d}x)$$

where $[p]$ is some multi-index, μ is Lebesgue measure on $\mathbb{R}^n$, the cartesian product of n copies of the real line $\mathbb{R}$, and f_p is the function

$$f_p : x \to r^{[p]} \exp(-x\,.\,r) \qquad x \in \mathbb{R}^n \qquad r \in (\mathbb{R}^+)^n$$

where $\mathbb{R}^+$ is the positive real line; T^p is a tempered distribution having bounded support on the left and the product $x\,.\,r$ is defined as

$$x\,.\,r = \sum_{i=1}^{n} x_i r_i.$$

Under this construction, the symmetry conditions on R will be inherited by the defining distribution T^p. Implicit in the remaining theory is that for a many-particle system the distribution T^p, associated with the radial part of the wavefunction, carries the appropriate symmetry constraints. In the examples, illustrating the method, only one-particle systems are considered, avoiding any symmetry complications.

The boundary condition that the wavefunction Ψ defines a bound state requires that Ψ be square integrable with respect to the volume element on $\mathbb{R}^n$. Taking the restriction to the radial part R of the wavefunction, the bound state condition requires that

$$R \in L^2((\mathbb{R}^+)^n, \nu)$$

where the measure ν on $(\mathbb{R}^+)^n$ is defined by

$$\nu(\mathrm{d}r) = \prod_{i=1}^{n} r_i^2 \, \mathrm{d}r_i.$$

A three-dimensional euclidean universe has been assumed. This is sufficient to guarantee that the trial wavefunctions used satisfy the hypotheses of the following lemmas, where

S^p and T^p will be tempered distributions having bounded support on the left, unless otherwise stated. Extensions of the proofs given in Farmer (1969) may be used to establish the results:

Lemma I: Given radial wavefunctions h_i, h_k such that

$$\langle h_i(r)|h_k(r)\rangle < \infty$$

then

$$\langle h_i(r)|h_k(r)\rangle = \langle S_x^p, \langle T_y^p, S_p^{xy}\rangle\rangle \equiv \langle S_x^p \otimes T_y^p, S_p^{xy}\rangle$$

where

$$h_i(r) = \langle S_x^p, f_p(x)\rangle \qquad h_k(r) = \langle T_y^p, f_p(y)\rangle$$

and

$$S_p^{xy} = \langle f_p(x)|f_p(y)\rangle.$$

Let $\mathscr{H}^l$ denote the Hamiltonian when Schrödinger's time-independent equation is reduced to radial dependence by a separation of variables technique, that is

$$\mathscr{H}^l R_k(r) = \lambda_{kp} R_k(r)$$

in which the associated eigenvalue λ_{kp} may depend on a parameter $[l]$, $[p] \equiv [p(l)]$ arising from the separation process. Then:

Lemma II: Using the above notation, but with $h_k \in \mathbb{D}_{\mathscr{H}^l} \subset L^2((\mathbb{R}^+)^n, v)$, $\mathbb{D}_{\mathscr{H}^l}$ the domain of the operator $\mathscr{H}^l$

$$\langle h_i(r)|\mathscr{H}^l|h_k(r)\rangle = \langle S_x^p, \langle T_y^p, H_p^{xy}\rangle\rangle$$

provided that T^p is a distribution having compact support and $[p] \geqslant 0$

$$h_k(r) = \langle T_y^p, f_p(y)\rangle$$

and

$$H_p^{xy} = \langle f_p(x)|\mathscr{H}^l|f_p(y)\rangle.$$

The generalization, when the Hamiltonian $\mathscr{H}$ for the system does not yield a radial Hamiltonian $\mathscr{H}^l$, uses a derived Hamiltonian $\mathscr{H}_{\text{der}}$, obtained by integrating out the angular dependence in the expression

$$\langle \Psi_i(r)|\mathscr{H}|\Psi_k(r)\rangle = \langle h_i(r)|\mathscr{H}_{\text{der}}|h_k(r)\rangle.$$

Modifying the definition of H_p to

$$H_p^{xy} = \langle f_p(x)|\mathscr{H}_{\text{der}}|f_p(y)\rangle$$

lemma II is valid under the more restrictive hypothesis that

$$\langle h_i(r)|\mathscr{H}_{\text{der}}|h_k(r)\rangle$$

is finite.

Both lemma II and its extension assume that the term arising from the potential energy operator does not imply the differentiation of negative powers of the radial co-ordinates.

3. Virial theory

The virial theorem for a particle, subject to a central attractive force ar^n, is

$$\langle T\rangle = \tfrac{1}{2}(n+1)\langle V\rangle$$

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the potential and kinetic energy operators respectively; for a hydrogen-like system, this reduces to

$$\langle V\rangle + 2\langle T\rangle = 0.$$

The form of the virial theorem may be modified to allow linear combinations of such central forces but, in other cases, the definition of the virial of the force may be used.

The Hamiltonian operator of a system having a classical analogue is the sum of the potential and kinetic energy operators. For such a system, a theory that allows for manipulation with the Hamiltonian will be sufficient for one dealing with the component operators. Then the pertinent building blocks are lemmas I and II. Otherwise, lemma II is sufficient to handle the kinetic energy term whilst the virial of the force may be handled directly in a given application.

Using the assumed decomposition of the wavefunction Ψ, the expectation value of the kinetic energy operator, $-\frac{1}{2}\nabla^2$, that is

$$\langle T\rangle \equiv \langle\Psi|-\tfrac{1}{2}\nabla^2|\Psi\rangle$$

becomes

$$\langle R(r)|-\tfrac{1}{2}\nabla_l^2|R(r)\rangle$$

to within a multiplicative constant, where ∇_l^2 defines the radial dependence of the kinetic energy operator, $[l]$ the parameter arising from the elimination of the angular dependence, $[p] \equiv [p(l)]$.

The radial function R may be expressed in the form

$$R(r) = \langle T_x^p, f_p(x)\rangle. \tag{2}$$

Hence, under the conditions of lemma II

$$\langle T\rangle = \langle T_x^p \otimes T_y^p, \langle f_p(x)|-\tfrac{1}{2}\nabla_l^2|f_p(y)\rangle\rangle$$

provided that T^p is a distribution having compact support and $[p]$ is a positive parameter.

Within this structure, the expectation value of the potential energy operator

$$\langle V\rangle \equiv \langle\Psi(\boldsymbol{r})|V|\Psi(\boldsymbol{r})\rangle$$

becomes

$$\langle R(r)|V_l(r)|R(r)\rangle.$$

This assumes that any angular dependence may be eliminated by integration and V_l denotes the derived radial dependence of the potential energy operator. Applying the definition (2) of R gives

$$\langle V\rangle = \langle T_x^p \otimes T_y^p, \langle f_p(x)|V_l(r)|f_p(y)\rangle\rangle.$$

Combining these results, the virial theorem reads

$$\langle T_x^p \otimes T_y^p, \langle f_p(x)|\nabla_l^2 + (n+1)V_l(r)|f_p(y)\rangle\rangle = 0$$

in the case of a central attractive force ar^n; for a hydrogen-like atom the form simplifies to

$$\langle T_x^p \otimes T_y^p, \langle f_p(x)|\nabla_l^2 - V_l(r)|f_p(y)\rangle\rangle = 0.$$

3.1. The hydrogen-like atom

Using the model of the three-dimensional hydrogen-like atom, the kinetic energy operator gives rise to the term

$$\nabla_l^2 = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{l(l+1)}{r^2}$$

whilst

$$V(r) \equiv V_l(r) = -\frac{Z}{r}.$$

An alternative procedure may be adopted by interpreting the radial equation

$$\left(-\frac{1}{2r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{Z}{r} + \frac{l(l+1)}{2r^2}\right)R_{ns}(r) = \lambda_{ns}R_{ns}(r)$$

as the one-dimensional motion of a particle in an effective potential energy V_l given by

$$V_l(r) = -\frac{Z}{r} + \frac{l(l+1)}{2r^2}$$

with

$$\nabla_l^2 = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right).$$

R_{ns} is the radial function associated with the eigenfunction Ψ_n defining the $(n-1)$th excited state, using a separation of variables. In the latter case, the generalized form of the virial theorem for central attractive forces ar^n is applicable.

In either treatment, the virial theorem for the hydrogen-like atom assumes the form

$$\left\langle T_x^{ns} \otimes T_y^{ns}, \int_0^\infty f(y, r, s)\exp\{-(x+y)r\}\,\mathrm{d}r \right\rangle = 0$$

where

$$f(y, r, s) = y^2 r^{2s+2} - 2y(s+1)r^{2s+1} + \{s(s+1) - l(l+1)\}r^{2s} + Zr^{2s+1}$$

and

$$R_{ns}(r) = \langle T_x^{ns}, f_s(x)\rangle.$$

A solution is given by choosing the arbitrary parameter s such that

$$s(s+1) - l(l+1) = 0$$

that is, $s = l$ or $-(l+1)$. The restriction that s must take a positive value forces the

choice $s = l$. If s is allowed to stand as a parameter, terms quadratic in $(x+y)$ are introduced. If the solution of the resulting equation is to satisfy Schrödinger's time-independent equation, s is forced to take the value substituted here. Hence

$$\left\langle T_x^{nl} \otimes T_y^{nl}, \int_0^\infty [y^2 r^{2l+2} + \{Z - 2y(l+1)\} r^{2l+1}] \exp\{-(x+y)r\}\, dr \right\rangle = 0.$$

It has been shown (Farmer 1969) to be sufficient to treat the distribution $T^{l+1,l} \equiv T^{l+1}$, which defines the lowest state for a given value l of the orbital quantum number, as a measure on some neighbourhood U_0 of the compact support of T^{l+1}. Then

$$\left\langle T_x^{l+1} \otimes T_y^{l+1}, \frac{(2l+1)!}{(x+y)^{2l+3}} \{Z(x+y) - 2xy(l+1)\} \right\rangle = 0.$$

Appealing to the bound-state boundary condition, $(x+y)^{-(2l+3)}$ is a positive integrable function on U_0. Elimination of the trivial solution leaves the condition

$$\{Z(x+y) - 2xy(l+1)\} T_x^{l+1} \otimes T_y^{l+1} = 0.$$

But T_x^{l+1} and T_y^{l+1} are identical, by construction, so that a solution is given by the equation

$$2x\{Z - (l+1)x\} T_x^{l+1} = 0$$

using the notation

$$T_x^{l+1} \otimes T_x^{l+1} \cong T_x^{l+1}.$$

Using the fundamental theorem (Schwartz 1966) that a distribution T on $\mathbb{R}$ satisfies

$$xT = 0$$

if and only if T is proportional to the Dirac measure δ having point support the origin

$$T^{l+1} \equiv 0 \qquad \text{or} \qquad T^{l+1} = C_{l+1} \delta_{Z/(l+1)}$$

for some constant C_{l+1}. Hence, a nontrivial solution is

$$R_{l+1,l}(r) = C_{l+1} r^l \exp\left(\frac{-Zr}{l+1}\right)$$

and the constant C_{l+1} may be determined from the normalization condition on the radial function $R_{l+1,l}$.

The excited states may be analysed by a combination of the above procedures and the treatment used in the discussion of excited states in the variational principle approach (Farmer 1969).

3.2. The Yukawa potential

An example in which the particle is subject to a central force not of the form ar^n, for some integer n, is provided by the Yukawa potential $-a \exp(-\lambda r) r^{-1}$. Using the definition of the virial of the force, the theorem reads

$$\langle -\nabla_l^2 \rangle = \left\langle r \frac{\partial V}{\partial r} \right\rangle$$

where the conservative force F on the particle is derivable from a potential energy function V

$$F = -\frac{\partial V}{\partial r}.$$

Insertion of the Yukawa potential yields

$$\langle -\nabla_l^2 \rangle = \left\langle ar\left(\frac{1}{r^2}+\frac{\lambda}{r}\right)\exp(-\lambda r)\right\rangle.$$

The inherent structure of the system is retained if only the spherically symmetric states are considered. A further simplification is introduced when the wavefunction Ψ_n, defining the $(n-1)$th excited state, is taken as

$$\Psi_n(r) \equiv R_n(r) = \langle T_x^n, f(x)\rangle$$

where T^n is a distribution having compact support and f is the function f_p, when p takes the value zero.

With this simple model, the necessary interchanges of integration in the final term may be justified directly. Applying the definition of Ψ_n, the theorem reads:

$$\left\langle T_x^n \otimes T_y^n, \frac{2xy}{(x+y)^3} - \frac{a(x+3\lambda+y)}{(x+\lambda+y)^3}\right\rangle = 0$$

which reduces to the appropriate equation for the spherically symmetric states of the hydrogen-like atom of nuclear charge a, in the limit $\lambda = 0$.

The standard arguments show that it is sufficient to consider the distribution T^1, defining the ground state, as a measure on some neighbourhood $\bar{U}$ of the compact support of T^1. Appealing to the boundary condition that Ψ_n defines a bound state and the inequality $\lambda \geqslant 0$, $(x+y)^{-3}.\ (x+\lambda+y)^{-3}$ is a positive integrable function on $\bar{U}$. Elimination of the trivial solution reduces the equation to

$$\{2(x+\lambda+y)^3xy - a(x+y)^3(x+3\lambda+y)\}T_x^1 \otimes T_y^1 = 0.$$

But, by construction, T_x^1 and T_y^1 are identical which implies that a solution is given by the equation

$$\{2x^2(2x+\lambda)^3 - a(2x)^3(2x+3\lambda)\}T_x^1 = 0$$

that is

$$2x^2 p(x, a, \lambda)T_x^1 = 0$$

where

$$T_x^1 \otimes T_x^1 \cong T_x^1.$$

The cubic $p(x, a, \lambda)$ has its stationary values given by the equation

$$12x^2 + 4x(3\lambda - 2a) + 3\lambda(\lambda - 2a) = 0$$

thus

$$x = \tfrac{1}{6}\{2a - 3\lambda \pm (6a\lambda + 4a^2)^{1/2}\}.$$

These stationary values are such that

$$x_s = (2a-3\lambda)+(6a\lambda+4a^2)^{1/2} \gtrless 0 \qquad \text{as} \qquad \lambda \lesseqgtr 2a.$$

Hence, for $\lambda > 2a$, both stationary points occur at negative values of x. Combining this with the knowledge that $p(-\infty, a, \lambda) \equiv -\infty$ and $p(0, a, \lambda) > 0$, the only zeros which occur take negative values and as such lead to physically unacceptable solutions.

For the reverse inequality $\lambda < 2a$, at least one stationary point occurs at a positive value of x. The facts that $p(-\infty, a, \lambda) \equiv -\infty$ and $p(0, a, \lambda) > 0$ couple to give at least one zero occurring at a negative value of x. The condition for three real zeros

$$p(\tfrac{1}{6}x_s, a, \lambda) < 0$$

reduces to the inequality

$$27\lambda^2 - 9a\lambda - 4a^2 - (2a + 3\lambda)(4a^2 + 6a\lambda)^{1/2} < 0$$

which is satisfied if

$$p_d(\lambda) \equiv 27\lambda^2 - 20a\lambda - 9a^2 < 0.$$

Estimating the quadratic p_d, $p_d(0) < 0$ whilst $p_d(2a) > 0$, that is, there exists some value $\lambda_c \in [0, 2a)$ such that $p_d(\lambda_c) = 0$ and hence the inequality is satisfied for all physically acceptable λ in the range $0 < \lambda < \lambda_c$. Solving for λ_c, subject to the condition $\lambda_c \in [0, 2a)$

$$\lambda_c = \frac{a}{27}(10 + 7\sqrt{7}).$$

Hence, for $(a/27)(10 + 7\sqrt{7}) < \lambda < 2a$, $p(x, a, \lambda)$ has only one real zero and this occurs at a negative value of x, yielding a physically unacceptable solution.

For the remaining range $0 < \lambda \leqslant \lambda_c$, the cubic p has three real zeros, either all distinct or where two may coincide; of these one occurs at a negative value of x, the remaining two (one) assuming positive values, since $p(0, a, \lambda) > 0$. Hence, if this particular inequality is satisfied by the pair λ, a, there exists either one or two points $x_c > 0$ such that

$$p(x, a, \lambda) \equiv (x - x_c)q(x, a, \lambda).$$

Then the equation defining the measure T^1 reads

$$2x^2(x - x_c)q(x, a, \lambda)T_x^1 = 0.$$

Ignoring the trivial solution and using the result quoted in the analysis of the hydrogen-like atom (Schwartz 1966)

$$T_x^1 = \delta_{x_c}$$

to within a multiplicative constant. Hence there exists an exponential function satisfying the virial theorem for the Yukawa potential when the parameters a and λ obey the above inequality. However, that a wavefunction satisfy the virial theorem is a necessary, but by no means sufficient, condition that it be an eigenfunction of the Schrödinger equation defining the system.

4. Hypervirial theory

Coulson (1965) has shown that if the Hamiltonian of a one-dimensional system H is given by

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + V(x)$$

and $|\Psi\rangle$ is a bound state eigenfunction for which

$$H|\Psi\rangle = \lambda_\Psi|\Psi\rangle$$

a necessary and sufficient condition for another exact bound state solution $|\Phi\rangle$

$$H|\Phi\rangle = \lambda_\Phi|\Phi\rangle$$

is that

$$\langle\Phi|[H, f(x)]|\Psi\rangle \equiv \langle\Phi|Hf(x)-f(x)H|\Psi\rangle = (\lambda_\Phi-\lambda_\Psi)\langle\Phi|f(x)|\Psi\rangle \tag{3}$$

for all suitably well behaved functions f. Parallel results are valid if the commutator $[H, f(x)]$ is replaced by either $[H, [H, f(x)]]$ or $[H, f(x)\,\mathrm{d}/\mathrm{d}x]$. The diagonal elements reduce to

$$\langle\Psi|[H, g]|\Psi\rangle = 0. \tag{4}$$

In generalizing hypervirial theory to the three-dimensional case, it is sufficient to work with a subspace invariant under the action of the Hamiltonian or a subspace containing all the bound-state eigenfunctions; a complete set of bound-state eigenfunctions $|\Phi\rangle$ will not exist always (Bradley and Hughes 1969). And Epstein and Hirschfelder (1961) give the theory where the function f is replaced by a time-independent operator W.

Since the distribution theory approach breaks down when the differentiation of negative powers of a coordinate is involved, only certain operators W are allowed but any analytic function is acceptable. Trouble will arise also when the double commutator $[H, [H, W]]$ is introduced. In some cases, this can be overcome by restricting attention to the spherically symmetric states (obviating the term $\frac{1}{2}l(l+1)r^{-2}$ occurring in the Legendrian) and expressing the kinetic energy operator in the form

$$\frac{-1}{2r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r.$$

This form follows naturally when the hermitian radial momentum operator proportional to

$$\frac{1}{r}\frac{\partial}{\partial r}r$$

is used in preference to the nonhermitian operator $\partial/\partial r$.

The first assumption is that any angular dependence in the expression

$$\langle\Phi(r)|[H, W]|\Psi(r)\rangle$$

may be integrated out; $[H, W]_{\mathrm{der}}$ is the radial operator derived from the commutator $[H, W]$ in the process.

Combining this with the modification necessary if the double commutator is used, lemmas I and II, previously established, are sufficient to justify the necessary interchanges of integration. The radial function R_{np} is associated with the eigenfunction Ψ_n, defining the $(n-1)$th excited state, in the separation of variables decomposition. Using the theory

$$R_{np}(r) = \langle T_x^{np}, f_p(x)\rangle$$

with T^{np} a distribution having compact support and $[p] \geqslant 0$. Then the diagonal hyper-

virial relation, derived from (4) when g is replaced by the operator W, yields the distributional hypervirial equation

$$\langle T_x^{np} \otimes T_y^{np}, \langle f_p(x)|[H, W]_{\text{der}}|f_p(y)\rangle\rangle = 0.$$

Generalizing to the off-diagonal case

$$\langle T_x^{np} \otimes T_y^{mp}, \langle f_p(x)|[H, W]_{\text{der}}|f_p(y)\rangle\rangle = C_{mn}(\lambda_{np} - \lambda_{mp})\langle T_x^{np} \otimes T_y^{mp}, \langle f_p(x)|W_{\text{der}}|f_p(y)\rangle\rangle$$

to within a multiplicative constant C_{mn}; W_{der} is the operator derived from W by the elimination of the angular dependence in the expression

$$\langle \Psi_n(r)|W|\Psi_m(r)\rangle$$

as above.

4.1. The hydrogen-like atom

The appropriate form of the hypervirial theory is the three-dimensional generalization where the angular dependence is eliminated, using the decomposition

$$\mathbb{R}^3 \cong \mathbb{R}^+ \otimes S^2$$

for S^2 the spherical shell parametrized by the pair (θ, ϕ). Then

$$\Psi_n(r) = R_{ns}(r) Y_l^m(\theta, \phi) \qquad s \equiv s(l)$$

is the decomposition for the wavefunction Ψ_n, defining the $(n-1)$th excited state, where $Y_l^m(\theta, \phi)$ denotes the spherical harmonic which is well defined for all values of the polar angle θ.

The derived Hamiltonian $\mathscr{H}^l$ is given by

$$\langle \Psi_n(r)|\mathscr{H}|\Psi_n(r)\rangle = C_s\langle R_{ns}(r)|\mathscr{H}^l|R_{ns}(r)\rangle$$

for some constant C_s.

The kinetic energy operator derived from $\mathscr{H}^l$ will be denoted by $-\frac{1}{2}\nabla_l^2$; any terms expressible as a function of r will be considered as contributing to the effective potential energy so that ∇_l^2 is simply the differential operator

$$\nabla_l^2 = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right).$$

Using Taylor's theorem in a neighbourhood of the origin for an analytic function f compatible with the hypervirial relations (3) and (4), $f(r) = r^m$, without loss of generality. Then the Hamiltonian $\mathscr{H}^l$ is such that

$$[\mathscr{H}^l, f] = -\tfrac{1}{2}[\nabla_l^2, f].$$

The decomposition

$$R_{ns}(r) = \langle T_x^{ns}, f_s(x)\rangle$$

holds for the radial function, T^{ns} a distribution with compact support and s a positive parameter. Then

$$\langle R_{ns}(r)|[\mathscr{H}^l, r^m]|R_{ns}(r)\rangle = \tfrac{1}{2}\left\langle T_x^{ns} \otimes T_y^{ns}, \frac{m\Gamma(m+2s+2)}{(x+y)^{m+2s+2}}(y-x)\right\rangle$$

where

$$\Gamma(z) = \int_0^\infty e^{-t} t^{z-1}\, dt \qquad \operatorname{Re} z > 0$$

and

$$\Gamma(z+1) = z\Gamma(z). \tag{5}$$

But, by construction, T_x^{ns} and T_y^{ns} are identical so that the diagonal hypervirial relation

$$\langle \Psi(\boldsymbol{r}) | [\mathscr{H}, f] | \Psi(\boldsymbol{r}) \rangle = 0$$

is trivially satisfied for $f(r)$ of the form r^m.

That either of the other two diagonal hypervirial relations quoted is valid for an infinity of functions f is a sufficient condition for the wavefunction Ψ to be an exact solution of the Schrödinger equation. Attention will be restricted to the one involving the double commutator. This necessitates the restriction to spherically symmetric states and the modified form of the kinetic energy operator. The hydrogen-like atom in three dimensions will be used to demonstrate the validity of the method whilst showing its impractibility as a means of solving the Schrödinger equation.

Without loss of generality, the function f will be defined as

$$f(r) = r^m$$

for some integer m. The assumption of spherical symmetry requires that

$$\Psi_n(\boldsymbol{r}) = R_n(r) = \langle T_x^n, \exp(-xr) \rangle$$

where T^n is a distribution having compact support. Then

$$\begin{aligned} &\langle \Psi_n(\boldsymbol{r}) | [\mathscr{H}, [\mathscr{H}, f(r)]] | \Psi_n(\boldsymbol{r}) \rangle \\ &\quad = \left\langle T_x^n \otimes T_y^n, \frac{m!}{4(x+y)^{m+1}} \{(m+1)(m-2)(x+y)^2 + 4Z(x+y) - 4xym(m-1)\} \right\rangle \\ &\quad = 0 \end{aligned}$$

since, for a diagonal hypervirial relation, the left hand side is zero.

It has been shown (Farmer 1969) to be sufficient to consider the distribution $T^{l+1,l} \equiv T^{l+1}$, defining the lowest state for a given value l of the orbital quantum number, as a measure on an arbitrary neighbourhood of the compact support of T^{l+1}. Taking the special case of spherical symmetry $l \equiv 0$, the distribution T^1 defining the ground state may be considered as a measure on an arbitrary neighbourhood of the compact support of T^1.

Appealing to the boundary condition that a bound state is defined by an L^2 eigenfunction, with respect to the measure $\nu(dr) = r^2$ on $\mathbb{R}^+$, establishes $(x+y)^{-(m+1)}$ as a positive integrable function on some neighbourhood $\overline{U}_0$ of the compact support of T^1. Elimination of the trivial solutions leaves the condition

$$\{(m+1)(m-2)(x+y)^2 + 4Z(x+y) - 4xym(m-1)\} T_x^1 \otimes T_y^1 = 0$$

for measure T^1. But, by construction, the measures T_x^1 and T_y^1 are identical so that, where T_x^1 denotes the diagonal tensor product $T_x^1 \otimes T_x^1$

$$x(Z-x) T_x^1 = 0.$$

Using the result from distribution theory quoted above

$$T_x^1 = C_1 \delta_Z$$

to within an arbitrary constant C_1, for nontrivial solution. Hence, the associated radial function is

$$R_1(r) = C_1 \exp(-Zr)$$

where a normalization condition on R_1 defines C_1 explicitly.

The excited states may be calculated by using (i) the orthogonality condition and the requirement that only pure states are considered to determine the form of the distribution and conditions on the support of any associated measure, and (ii) the hypervirial relation and symmetry arguments to determine the specific measure; but only the spherically symmetric terms are amenable to this procedure.

But the off-diagonal hypervirial relations also provide sufficient conditions for the solution of the Schrödinger equation. The simplest form of function f, compatible with the theory, will be assumed, that is

$$f(r) = r^m$$

without loss of generality. States having distinct values of the orbital quantum number l, and hence $s \equiv s(l)$, will lead to trivial relations, from the orthogonality of the functions defining the angular dependence. Hence, using the functional equation (5), one derives the hypervirial relation

$$\left\langle T_x^{ns} \otimes T_y^{ks}, \frac{\Gamma(m+2s+2)}{(x+y)^{m+2s+3}} \{\tfrac{1}{2}(y-x)(x+y)m - (m+2s+2)(\lambda_n - \lambda_k)\} \right\rangle = 0$$

from the form

$$\langle \Psi_n(r) | [\mathscr{H}, r^m] | \Psi_k(r) \rangle = (\lambda_n - \lambda_k) \langle \Psi_n(r) | r^m | \Psi_k(r) \rangle.$$

The off-diagonal hypervirial method assumes a knowledge of the lowest state, for fixed l, that is

$$T^{l+1,l} = \delta_{Z/(l+1)}$$

to within a multiplicative constant, with

$$2\lambda_{l+1,l} = -Z^2(l+1)^{-2}.$$

As for the variational principle, the orthogonality condition establishes that $T^{l+2,l} \equiv T^{l+2}$ is a distribution of the first order. The requirement that only pure states are considered combines to give the decomposition of T^{l+2} on a neighbourhood of the compact support of T^{l+2} as

$$T^{l+2} = (1 - A^l D)\mu_1^l$$

for some constant A^l and measure μ_1^l. Working on some neighbourhood W for which this decomposition of T^{l+2} is valid, the off-diagonal relation, associating the two lowest states for a given l, is

$$\left\langle \mu_1^l, r(x, m, s, \lambda_{l+2,l}) \left(x + \frac{Z}{l+1} \right)^{-\beta} \right\rangle = 0$$

for some function r, where $\beta = m + 2s + 4$.

But the orthogonality condition gives μ_1^l as the Dirac measure δ_w on some $\overline{W}$, where

$$w+\frac{Z}{l+1}-(2s+3)A^l = 0.$$

The equation then reduces to

$$m^2A^l(\tfrac{1}{2}w^2+\lambda_{l+2,l})-mA^l\left\{w\left(w+\frac{Z}{l+1}\right)-(s+1)\left(\frac{Z^2}{(l+1)^2}+2\lambda_{l+2,l}\right)\right\} = 0.$$

This holds for all m, and hence for an infinity of functions f, if

$$\text{(i)}\quad w^2+2\lambda_{l+2,l} = 0 \tag{6}$$

and

$$\text{(ii)}\quad w^2+\frac{Zw}{l+1}-(s+1)\frac{Z^2}{(l+1)^2}-2(s+1)\lambda_{l+2,l} = 0.$$

Eliminating $2\lambda_{l+2,l}$ between these equations gives

$$w = \frac{Z(s+1)}{(l+1)(s+2)} \qquad \text{or} \qquad -\frac{Z}{l+1}.$$

The second choice is incompatible with the condition that the support of the measure μ_1^l, that is, supp μ_1^l, is such that

$$\text{supp}\,\mu_1^l \subseteq \mathbb{R}^+.$$

The value of the constant A^l may be calculated from the orthogonality conditions, thus

$$A^l = \frac{Z}{(l+1)(s+2)}.$$

In previous estimates of the excited states, the choice

$$s = l$$

has already been forced at this stage. In this treatment, substitution in the Schrödinger equation forces the same choice to eliminate the term arising from the angular dependence. Then w and A^l may be computed and condition (6) gives the energy eigenvalue $\lambda_{l+2,l}$ as

$$2\lambda_{l+2,l} = -Z^2(l+2)^{-2}.$$

With the knowledge of A^l, w and μ_1^l already acquired, T^{l+2} is then determined explicitly, together with the value of the energy eigenvalue.

But reference has been made to the Schrödinger equation to define a suitable choice for the arbitrary parameter s. This difficulty would have been obscured had the decomposition

$$\Psi_n(r) = R_{nl}(r)Y_l^m(\theta,\phi)$$

been assumed initially. Proceeding similarly, higher excited states may be evaluated.

5. Conclusions

Whereas the distribution function approach has shown the existence of an exponential function satisfying the virial theorem for the Yukawa potential for a restricted range of the defining parameters, the heavy equations involved in any treatment of the hypervirial relations would make the method seem to be of theoretical, rather than practical, relevance there.

Acknowledgments

The author wishes to thank Professor C A Coulson for his suggestion of investigating the application of distribution theory to virial theory.

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