The Virial Theorem for Non-Coulombic Interactions and Scaled Approximate Wave Functions

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The virial theorem for various not necessarily homogeneous potential functions $V(r)$ is derived. It is proved in a transparent way that approximate wave functions at optimal scale satisfy the general virial theorem for any radial potential $V(r)$. The proposed method for improving a variational wave function which by the scaling procedure obeys the virial theorem is tested in the case of some simple screened coulomb potentials.

Das Virialtheorem für verschiedene, nicht unbedingt homogene Potentialfunktionen $V(r)$ wird abgeleitet. Es wird gezeigt, daß eine Näherungsfunktion mit optimalem Skalen-parameter auch das allgemeine Virialtheorem für beliebige Radialpotentiale $V(r)$ erfüllt. Die Methode der Streckung des Grundgebietes (scaling) dient zur Verbesserung von Näherungs-funktionen, was am Beispiel einiger abgeschirmter Coulomb-Potentiale demonstriert wird.

Le théorème du viriel pour quelques fonctions de potentiel $V(r)$ non nécessairement homo-gènes est dérivé du théorème général. Il est prouvé d'une manière intuitive que des fonctions d'onde approchées, à l'échelle optimum, satisfont le théorème du viriel général pour tous les potentiels radiaux $V(r)$. La méthode proposée pour améliorer une fonction d'onde variation-nelle, qui obéit au théorème du viriel, est essayée dans le cas de quelques simples potentiels coulombiens écrantés.

I. Introduction

Fock's [1] derivation of the quantum mechanical virial theorem from the variation principle depends upon the homogeneity of the potential energy function $V(r) \sim r^n$. The method of dimensions allows the expectation values of the kinetic and potential energy with respect to scaled functions to be expressed by functions of the scale $\eta = 1$:

$$\langle T \rangle_\eta = \eta^2 \langle T \rangle$$
$$\langle V \rangle_\eta = \eta^{-n} \langle V \rangle . \tag{1}$$

Here $\langle \rangle_\eta$ denotes a mean value calculated from scaled functions $\varphi_\eta = \eta^{3N/2} \varphi (\eta \boldsymbol{r})$, N is the number of electrons, and $\langle \rangle$ is the respective value for corresponding unscaled functions $\varphi(\boldsymbol{r})$. The minimization of the total energy E_η leads to an optimal η_0

$$\eta_0^{n+2} = \frac{n \langle V \rangle}{2 \langle T \rangle} \tag{2}$$

which yields the virial theorem, if in fulfilment of the variation principle, η_0 is equal to unity for the exact solution φ.

More important is the fact that any approximate function at optimal scale also fulfils the virial theorem

$$\langle T \rangle_\eta = \frac{n}{2} \langle V \rangle_\eta$$

or

$$\eta^2 \langle T \rangle = \frac{n}{2} \eta^{-n} \langle V \rangle \tag{3}$$

which follows from inserting η_0 of Eq. (2) in Eq. (1). Because of the arbitrariness of the approximate trial function the function φ_η at optimal scale may still be far from the correct solution [2, 3]. However, if the trial function is an exact solution of a similar system, it can be expected at optimal scale to be a good approximation also for a perturbed problem. In this case by optimal scaling an improvement of the wave functions is obtained which then necessarily satisfy the virial theorem [4, 5].

This paper is not concerned with simple homogeneous potential energy functions but covers various non-coulombic potentials by deriving their virial theorems and investigating approximate functions at optimal scale for more complicated interactions for which the Schrödinger equation is not solvable [6]. We are interested in improving approximate wave functions by scaling them so that they satisfy the corresponding virial theorem. The potentials investigated are applicable to interactions between electrons and nuclei but also are used in the meson theory of nuclear forces. Therefore, these potentials may act as screened potentials in the theory of atoms, molecules and of the solid state, while functions having a singularity may describe also scattering potentials. A potential which is of our particular concern is the well known Debye-Hückel or Yukawa potential $e^{-\alpha r}/r$. First we shall prove the statement which is given in the subsequent headline.

II. Scaled Wave Functions Satisfy the General Virial Theorem for Any Potential $V(r)$

For a non homogeneous potential function Fock's [1] procedure cannot be followed since for this case it is not possible to resolve the expectation values with respect to scaled functions in the way shown in Eq. (1). However, the general virial theorem is

$$2\langle T \rangle = - \langle W \rangle \tag{4}$$

in which W is the Clausius virial of forces

$$W = \sum_i x_i F_i \tag{5}$$

$$F_i = - \frac{\partial V}{\partial x_i} \tag{6}$$

where the summation runs over all coordinates of each particle. In Eq. (4) the form of the potential function V is not specified. If we consider only the radial part of the potential $V = V(r)$, which for the present purpose is no loss of generality, the virial theorem is more conveniently written as

$$2\langle T \rangle = \langle r \frac{dV}{dr} \rangle \ . \tag{7}$$

It is now easy to show that this equation holds also if the integrals are calculated from approximate functions at optimal scale. The energy minimization for scaled functions

$$E_\eta = \langle T \rangle_\eta + \langle V \rangle_\eta = \eta^2 \langle T \rangle + \langle V \rangle_\eta \tag{8}$$

$$\frac{\partial E_\eta}{\partial \eta} = 2\eta \langle T \rangle + \frac{\partial \langle V \rangle_\eta}{\partial \eta} = 0 \tag{9}$$

leads to the following condition

$$2\,\eta^2 \langle T \rangle = -\eta \, \frac{\partial \langle V \rangle_\eta}{\partial \eta} \, . \tag{10}$$

It is shown in the appendix that the right hand side can be rewritten

$$-\eta \, \frac{\partial \langle V \rangle_\eta}{\partial \eta} = \langle r \frac{dV}{dr} \rangle_\eta, \tag{11}$$

so that the minimum condition, Eq. (10), is identical with

$$2\eta^2 \langle T \rangle = \langle r \frac{dV}{dr} \rangle_\eta \tag{12}$$

which actually is the virial theorem Eq. (7) for optimal scaled approximate functions. The relation which is the key to the proof of Eq. (11) is

$$\frac{dV}{dr} = \eta \left(\frac{\partial V}{\partial \varrho} \right)_\eta = -\frac{\eta^2}{\varrho} \left(\frac{\partial V}{\partial \eta} \right)_\varrho \tag{13}$$

if the substitution $\varrho = \eta r$ is applied.

The identity of Eq. (10) and (12) shows in a transparent way that approximate wave functions at optimal scale satisfy the virial theorem for any radial- and not necessarily homogeneous potential function.

By a proper choice of the hypervirial generator function which leads to the usual virial theorem it also can be shown without specifying the potential that a variational wave function satisfies the virial theorem if the necessary point transformation is a coordinate scaling [7, 8]. The connection of the energy minimization and the virial theorem for scaled functions is, however, not given in such a straightforward way.

III. The Virial Theorem for Various Potentials as Derived from Eq. (7)

In this section some virial theorems of various potentials are derived which are of general physical interest. Since there is only a differentiation occurring in the general theorem Eq. (7) it is possible in principle to derive virial theorems for all differentiable potential functions.

A) The Screened Potential $V(r) = r^n e^{-\alpha r^m}$ (n, m, α Real Numbers)

Its first derivative is given by

$$\frac{dV(r)}{dr} = nr^{n-1} e^{-\alpha r^m} - \alpha \, mr^{n+m-1} e^{-\alpha r^m}$$

$$= V(r) (nr^{-1} - \alpha \, mr^{-1}) \tag{14}$$

which leads to the virial theorem

$$2 \langle T \rangle = n \langle V \rangle - \alpha \, m \langle r^m V \rangle \, . \tag{15}$$

This potential function may act as a scattering potential. In its attractive form it is the Yukawa potential (for $n = -1$, $m = 1$) which also was used as screened potential in atomic, molecular and solid state theory [9]. Such a potential does not necessarily lead to a bound state. The critical value of n for the existence of a stable or unstable state lies about $n = -2$ [10, 11]. However, also the value of α should influence the number of states substantially which can be filled into this potential well.

B) The Generalized Slater Screened Potential $V(r) = A/r^a + B/r^b$

This type of potential is a superposition of two homogeneous potentials

$$V(r) = V_a(r) + V_b(r) .\tag{16}$$

Since the differentiation is a linear operator, the virial theorem is simply given from Eq. (1) and (7) by the sum

$$2 \langle T \rangle = - a \langle V_a \rangle - b \langle V_b \rangle .\tag{17}$$

The potential B also is used as a scattering potential [12].

C) The Oscillating Potential $V(r) = r^n \sin (ar) e^{-\alpha r}$

$$r \frac{dV}{dr} = V[n + ar \operatorname{ctg} (ar) - \alpha r]\tag{18}$$

leads to the virial theorem

$$2 \langle T \rangle = n \langle V \rangle + a \langle rV \operatorname{ctg} (ar) \rangle - \alpha \langle rV \rangle .\tag{19}$$

Similarly the hyperbolic function

$$V(r) = r^n \sinh (ar)\tag{20}$$

has the virial theorem

$$2 \langle T \rangle = n \langle V \rangle + a \langle r^{n+1} \cosh (ar) \rangle .\tag{21}$$

It is noticed that all potentials considered lead to a virial theorem which is identical with that for homogeneous functions except for additional terms. Also, for aniso-tropic potentials like $= \dfrac{1}{\sqrt{x^2 + y^2 + cz^2}}$ the virial theorem is formally identical with that of the coulombic case $2 \langle T \rangle = - \langle V \rangle$. The series of virial theorems which are easily derived from Eq. (7) can be continued at length. However, most of them one may construct will lack physical application. We shall rather return to the screened coulomb potential of type A and investigate for certain examples the behavior of scaled approximate functions.

IV. Scaled Wave Functions Serve as Approximations for Non-Solvable Schrödinger Potentials

An approximate variational function satisfying the virial theorem is not necessarily close to the exact solution. As it was already mentioned in the intro-duction, we may expect, however, a wave function which is an exact or a good solution for a neighboring problem to be also an acceptable solution for any per-turbed system. If we furthermore choose the function at optimal scale the solution should be improved according to the variation principle.

Let us consider as an example some screened atomic coulomb potentials which are not accurately solvable but from where we know the exact solutions of a similar,

i.e. the coulomb problem. In the table the results are given for several potentials of this type with varying parameters. The optimal scaling parameters and the minimal energy values are calculated from a scaled hydrogen $1s$ function $\psi_\eta = 2\eta^{3/2} e^{-\eta r}$ This function is considered to be an approximation for the ground states, which should be particularly good for screened potentials close to the coulomb case (α or C small).

Table. *Optimal scaling parameters and ground state energies for several Schrödinger potentials calculated from a scaled 1s hydrogen function*

potential $V(r)$	parameter	η_0	$E_{\min}$	$\langle V \rangle$ [a]
$-\dfrac{e^{-\alpha r}}{r}$	$\alpha = 1.0$	0.5000	0	-0.125
	$\alpha = 0.5$	0.8735	-0.1465	-0.5280
	$\alpha = 0.2$	0.9757	-0.3268	-0.8028
	$\alpha = 0$	1.0	-0.5	-1.0
$-\dfrac{e^{-\alpha r}}{r^2}$	$\alpha = 1.0$	0.5486	-0.1646	-0.3150
	$\alpha = 0.5$	0.2743	-0.0411	-0.0787
	$\alpha = 0.2$	0.1097	-0.0066	-0.0126
$-\dfrac{1}{r} + \dfrac{C}{r^2}$	$C = 1.0$	0.2000	-0.1000	-0.1200
	$C = 0.5$	0.3333	-0.1667	-0.2222
	$C = 0.2$	0.5556	-0.2778	-0.4321
	$C = 0.1$	0.7143	-0.3571	-0.6122

[a] Expectation value of the potential energy; that of kinetic energy is given by $\frac{1}{2}\eta_0^2$.

Concentrating our attention on the Yukawa potential we find already for small α a substantial increase in the total energy as compared to the coulomb case. This is predominantly due to the change in potential energy, the kinetic energy being almost constant. This behaviour is quite different to that expected from the coulombic virial theorem according to which the change in potential energy caused by the perturbation is $\Delta \langle V \rangle = -2\Delta \langle T \rangle$. A similar result is obtained for the screened Slater potential $-1/r + C/r^2$. In this case the change of kinetic energy is, however, larger than calculated from the coulombic formula. The assumption that an additional node plane e.g. when going from certain Slater functions to hydrogen-like functions, increases the kinetic orbital energy is not necessarily true because the virial theorem for different potentials affects the kinetic part differently. The potentials considered represent real screening effects on the nuclear charge, because in either case the functions are expanded by virtue of the scaling factor $\eta < 1$, which also gives rise to smaller Slater-Condon parameters. In the formulas derived in this paper the $1/r_{ij}$ operator of the potential function was not taken into account explicitly. It formally can be considered but its inclusion, however, does not give rise to new aspects for the problems discussed here. This is equally true for an extension of the present procedure to molecular systems. The other potential $e^{-\alpha r}/r^2$ which was included in the table is not a screened coulomb potential. The hydrogen functions are therefore expected not to be good approximations and the scaling parameter does not approach the coulomb limit

for small α. Nothing can be said about the quality of this approximation since correct solutions are missing for such a type of interaction.

V. Appendix

Substituting $\varrho = \eta r$ the expectation value of the potential part of energy calculated from the scaled function is given by

$$\langle V \rangle_\eta = \int_0^\infty \psi(\varrho) \; V(\varrho/\eta) \; \psi(\varrho) \; \varrho^2 \; d\varrho \; . \tag{22}$$

Let

$$\int \psi(\varrho) \; V(\varrho/\eta) \; \psi(\varrho) \; \varrho^2 \; d\varrho = f_1(\varrho, \eta) \tag{23}$$

without integration limits. Then we call the integrand of Eq. (22)

$$\left(\frac{\partial f_1}{\partial \varrho} \right)_\eta = f_2(\varrho, \eta) \; , \tag{24}$$

its derivative with respect to η is

$$\left(\frac{\partial f_2}{\partial \eta} \right)_\varrho = \psi(\varrho) \left(\frac{\partial V(\varrho/\eta)}{\partial \eta} \right)_\varrho \psi(\varrho) \; \varrho^2 \; . \tag{25}$$

We further define

$$\left(\frac{\partial f_1}{\partial \eta} \right)_\varrho = f_3(\varrho, \eta) \tag{26}$$

which is connected to $\langle V \rangle_\eta$ by

$$\frac{\partial \langle V \rangle_\eta}{\partial \eta} = f_3(\infty, \eta) - f_3(0, \eta) \; . \tag{27}$$

When commuting the differentiation we have

$$\left(\frac{\partial f_2}{\partial \eta} \right)_\varrho = \left(\frac{\partial f_3}{\partial \varrho} \right)_\eta = \frac{\partial^2 f_1}{\partial \varrho \partial \eta} \; . \tag{28}$$

From Eq. (13) it is obtained

$$\left(\frac{\partial V}{\partial \eta} \right)_\varrho = -\frac{\varrho}{\eta} \left(\frac{\partial V}{\partial \varrho} \right)_\eta \; . \tag{29}$$

Inserting this in Eq. (25) yields

$$\left(\frac{\partial f_2}{\partial \eta} \right)_\varrho = -\frac{1}{\eta} \psi(\varrho) \; \varrho \left(\frac{\partial V}{\partial \varrho} \right)_\eta \psi(\varrho) \varrho^2 \; . \tag{30}$$

Together with Eq. (28) the right hand side is after integration over ϱ

$$-\frac{1}{\eta} \int \psi(\varrho) \; \varrho \left(\frac{\partial V}{\partial \varrho} \right)_\eta \psi(\varrho) \; \varrho^2 \; d\varrho = f_3(\varrho, \eta)$$

or with the integration limits

$$-\frac{1}{\eta} \int_0^\infty \psi(\varrho) \; \varrho \left(\frac{\partial V}{\partial \varrho} \right)_\eta \psi(\varrho) \; \varrho^2 \; d\varrho = f_3(\infty, \eta) - f_3(0, \eta) \tag{31}$$

which leads when comparing with Eq. (27) to the desired formula

$$-\eta \frac{\partial \langle V \rangle_\eta}{\partial \eta} = \int_0^\infty \psi(\varrho) \; \varrho \left(\frac{\partial V}{\partial \varrho} \right)_\eta \psi(\varrho) \; \varrho^2 \; d\varrho = \langle r \frac{\partial V}{\partial r} \rangle_\eta$$

after resubstitution of $\varrho = \eta r$. Effectively it is therefore possible to exchange the differentiation to η and the integration over ϱ and consider the integrand as a function of the two independent variables η and ϱ.

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