ONE-DIMENSIONAL HYPERVIRIAL THEOREMS IN DENSITY FUNCTIONAL THEORY

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For a restricted class of operators hypervirial theorems are established involving wavefunctions ψ_i for N fermions which move independently in a common external one-dimensional potential $V(x)$. Using this class it is possible to perform the summation over states ψ_i yielding exact relations between ground state density ρ and kinetic energy density ϵ_k and potential $V(x)$. It is checked to what extent the Thomas–Fermi expressions for ρ and ϵ_k satisfy these relations.

1. Hypervirial theorems (HVTs) involving single stationary states have been established and applied since 1960 up to the present; an incomplete list of references is given by refs. [1–16]. These theorems are based on the fact that for arbitrary operators $\hat{A}$

$$J[\psi|\hat{A}] \equiv \langle\psi|[\hat{H},\hat{A}]|\psi\rangle = 0 , \tag{1}$$

if $|\psi\rangle$ is an exact solution of the stationary Schrödinger equation $\hat{H}|\psi\rangle = E|\psi\rangle$. When $\hat{A}$ is specified the commutator can be calculated explicitly so that eq. (1) becomes a relation which may be used e.g. as a condition to be imposed on approximate wavefunctions. For $\hat{A} = \hat{x}\hat{p}$ the well-known quantum mechanical virial theorem is obtained, see e.g. ref. [17].

It is the purpose of the present letter to set up corresponding relations not for single states but for ground state particle density ρ and kinetic energy density ϵ_k as used in density functional theories. In this work we only treat one-dimensional systems of fermions moving in a common one-body potential $V(x)$. All calculations are performed in the position representation.

The general procedure of finding HVTs for ρ and ϵ_k is as follows:

(i) Choosing convenient operators $\hat{A}$.

(ii) Deriving for each $\hat{A}$ chosen a HVT satisfied by the wavefunctions $\langle x|\psi_i\rangle = \psi_i(x)$.

(iii) Summing over ψ_i.

(iv) Eliminating the sums involving ψ_i by ρ, ϵ_k and their derivatives with respect to x.

At first sight numerous HVTs seem to be possible

due to the unbounded number of choices of $\hat{A}$. There are, however, several restrictions to be imposed on these operators so that the number of nontrivial HVTs is reduced considerably.

(i) All those $\hat{A}$ have to be discarded which make $\langle\phi|[\hat{H},\hat{A}]|\phi\rangle$ vanish even if $\phi(x)$ is not an eigenfunction of $\hat{H}$. Otherwise the corresponding HVT contains no nontrivial information.

Let us give a simple criterion sufficient for elimination of those operators $\hat{A}$. When ϕ and $\phi' \equiv d\phi/dx$ vanish rapidly enough at the limits a, b of integration (usually $a = -\infty$, $b = +\infty$) $\hat{H}$ is hermitean with respect to ϕ so that

$$J[\phi|\hat{A}] = \int_a^b \phi^*(\hat{H}\hat{A} - \hat{A}\hat{H})\phi \, dx ,$$

$$= \int_a^b [(\hat{H}\phi)^*(\hat{A}\phi) - (\hat{H}\phi)(\hat{A}^+\phi)^*] \, dx .$$

When ρ, ϵ_k is to be calculated it is always possible to choose the set of eigenfunctions ψ_i real, so that

$$\rho(x) = 2\sum_{i=1}^{N/2} \psi_i^2(x) , \tag{2}$$

$$\epsilon_k(x) = 2\sum_{i=1}^{N/2} \frac{\hbar^2}{2m}\psi_i'^2(x) , \tag{3}$$

where N is the (even) number of particles occupying the lowest $N/2$ levels twice each. Therefore, when we

confine ourselves to use real ϕ, too, it follows, due to the reality of $\hat{H}$, that

$$J[\phi|\hat{A}] = \int_a^b (\hat{H}\phi)\,[(\hat{A} - \hat{A}^{+*})\,\phi]\;\mathrm{d}x\,,$$

which vanishes if

$$\hat{A} = \hat{A}^{+*}\,, \tag{4}$$

irrespective of whether ϕ is an eigenfunction of $\hat{H}$ or not. Thus operators $\hat{A}$ obeying eq. (4) have to be eliminated. A special case of (4) which has also been mentioned by Epstein and Hirschfelder [2] is given by real hermitean operators $\hat{A}$.

Let e.g. $\hat{A} = \hat{p}^s$, where $s \geqslant 0$ is an integer and $\hat{p} = -i\hbar \mathrm{d}/\mathrm{d}x$. If s is even $\hat{A}$ satisfies eq. (4) and thus yields $J[\phi|\hat{p}^s] = 0$ for all ϕ. If, however, s is odd, $\hat{A}$ satisfies $\hat{A} = -\hat{A}^{+*}$ and therefore can be used for HVTs, unless J vanishes by symmetry. This happens for potentials V of even parity because then $[\hat{H}, \hat{p}^s]$ (s odd) has odd parity so that $J[\phi|\hat{p}^s]$ must be zero for any trial function ϕ with definite parity. Thus HVTs derived from $\hat{A} = \hat{p}^s$, e.g. eq. (16) for $s = 1$ (see below), are non-trivial for all potentials except for those having even parity.

(ii) $\hat{A}$ has to be chosen so that it is possible to eliminate sums involving ψ_i and their derivatives by ρ, ϵ_k and/or their derivatives. This is a very severe restriction. If e.g. a sum $\sum_{i=1}^{N/2} (\psi_i'')^2$ appears under the integral sign it cannot be expressed by $\rho, \rho', \rho'' \dots$ or $\epsilon_k, \epsilon_k', \dots$ or combinations thereof.

(iii) Only $\hat{A}$'s linear independent of each other are to be used. If e.g. $\hat{A}_1 \equiv \hat{p}, \hat{A}_2 \equiv \hat{p}^2\hat{x}$ have been used the operator

$$\hat{A}_3 \equiv \hat{p}\hat{x}\hat{p} = \hat{A}_2 + i\hbar\hat{A}_1$$

clearly cannot yield any new information.

It is sufficient to deal with operators $\hat{A}$ having the structure $\hat{f}\hat{g}$ where $\hat{f}, \hat{g}$ are arbitrary operator functions of $\hat{x}$ and $\hat{p}$, respectively.

2. The method described and discussed generally above is now applied to some operators having the more restricted form

$$\hat{A} = \hat{f}(x)\hat{p}^s \quad (s \geqslant 0 \text{ integer})\,, \tag{5}$$

where $\hat{f}(x)$ is still arbitrary. In what follows it is supposed that all integrated terms emerging from integration by parts vanish since the ψ's and their derivatives do at the limits. Let us investigate HVTs correspond-

ing to the first few values of s. Using the hamiltonian

$$\hat{H} = \hat{p}^2/2m + \hat{V}(x) \tag{6}$$

we obtain

$$[\hat{H}, \hat{A}] = -(i\hbar/m)\,\hat{f}'\hat{p}^{s+1} - (\hbar^2/2m)\,\hat{f}''\hat{p}^s$$

$$+ \hat{f}[\hat{V}, \hat{p}^s]\,. \tag{7}$$

(i) $s = 0$: From $\hat{f}^+ = \hat{f}^*$ it follows that

$$\hat{A}^{+*} = \hat{f}^{**} = \hat{f} = \hat{A}\,. \tag{8}$$

Therefore, according to the criterion given above, the case $s = 0$ does not yield results selective for eigenfunctions of $\hat{H}$, see also ref. [1].

(ii) $s = 1$: Hypervirial operators $\hat{A} = \hat{f}\hat{p}$, especially $\hat{x}^N\hat{p}$ ($N \geqslant 0$ integer), have been used most commonly in one-dimensional problems, see ref. [7–16], where exact results on eigenvalues, matrix elements $\langle\psi|\hat{x}^N|\psi\rangle$ and local values of wavefunctions have been obtained.

Fortunately, this type of operators also allows for deriving relations between ρ, ϵ_k and/or their derivatives.

When the commutator $[\hat{H}, \hat{f}\hat{p}]$ is inserted in eq. (1), we obtain

$$J[\psi|\hat{f}\hat{p}] = \frac{i\hbar^3}{m}\left(\int_a^b \psi f'\psi''\;\mathrm{d}x + \tfrac{1}{2}\int_a^b \psi f''\psi'\;\mathrm{d}x\right)$$

$$+ i\hbar \int_a^b \psi f V'\psi\;\mathrm{d}x\,. \tag{9}$$

Note that ψ is chosen real. Let us denote the kinetic energy density t of a single wavefunction by

$$t \equiv (\hbar^2/2m)(\psi')^2\,, \tag{10}$$

and integrate the first two integrals in eq. (9) by parts so that no derivatives of f occur any longer in the integrals. From eqs. (1) and (9) it follows that

$$\int_a^b f[-4t' + (\hbar^2/2m)(\psi^2)''' - 2V'\psi^2]\;\mathrm{d}x = 0\,. \tag{11}$$

However, f was an arbitrary function. Therefore eq. (11) can be valid only if

$$4t' = (\hbar^2/2m)(\psi^2)''' - 2V'\psi^2\,. \tag{12}$$

When we replace ψ by ψ_i and sum over i, we obtain from eqs. (2), (3), and (11)

$$\epsilon_k'(x) = (\hbar^2/8m)\,\rho'''(x) - \tfrac{1}{2}V'(x)\rho(x)\,. \tag{13}$$

This relation is exact for exact ρ and ϵ_k. A corresponding result has been found in quite another way by March and Young [18], where these authors, however, use a definition of ϵ_k which differs from our ϵ_k by a divergence term. It should be noted that eq. (11), and therefore also (12) and (13) turn out to be valid even if the integrated parts which occur in the derivation of (11) from (9) do not vanish separately. In this case they cancel, however, against the right-hand side of eq. (1) which is now given by

$$(i\hbar^3/2m) \left[\psi(f\psi')' - f(\psi')^2\right]_{x=a}^{x=b} .$$

Integrating eq. (13) we obtain

$$\epsilon_k(x) = \epsilon_k(a) + (\hbar^2/8m) \left[\rho''(x) - \rho''(a)\right]$$
$$- \tfrac{1}{2} \int_a^x V'(\xi)\, \rho(\xi)\, \mathrm{d}\xi . \tag{14}$$

When it is assumed that ϵ_k, ρ and its derivatives vanish at the limits a, b it follows that

$$\epsilon_k(x) = (\hbar^2/8m)\, \rho''(x) - \tfrac{1}{2} \int_a^x V'(\xi)\rho(\xi)\, \mathrm{d}\xi , \tag{15}$$

and

$$\int_a^b V'(\xi)\rho(\xi)\, \mathrm{d}\xi = 0 . \tag{16}$$

The total kinetic energy T is then given by

$$T = \int_a^b \epsilon_k(x)\, \mathrm{d}x = -\tfrac{1}{2} \int_a^b \mathrm{d}x \int_a^x V'(\xi)\rho(\xi)\, \mathrm{d}\xi$$
$$= -\tfrac{1}{2} \left[x \int_a^x V'(\xi)\rho(\xi)\, \mathrm{d}\xi\right]_{x=a}^b$$
$$+ \tfrac{1}{2} \int_a^b x V'(x)\rho(x)\, \mathrm{d}x ,$$

i.e. we obtain the well-known virial theorem

$$T = \tfrac{1}{2} \int_a^b x V'(x)\rho(x)\, \mathrm{d}x \tag{17}$$

on account of (16). Thus eq. (15) is a "differential" virial theorem, i.e. a relation being valid pointwise.

From the differential virial theorem we can derive a whole sequence of special relations by calculating moments of ϵ_k. For instance, multiplying (15) with x^2 and integrating by parts yields

$$\int_a^b x^2 \epsilon_k\, \mathrm{d}x = (\hbar^2/4m)\, N + \tfrac{1}{6} \int_a^b x^3 V'\rho\, \mathrm{d}x . \tag{18}$$

Similarly we obtains

$$\tfrac{2}{3} \int_a^b x^3 \epsilon_k\, \mathrm{d}x = \frac{\hbar^2}{2m} \int_a^b x\rho\, \mathrm{d}x + \tfrac{1}{12} \int_a^b x^4 V'\rho\, \mathrm{d}x , \tag{19}$$

thus relating ϵ_k and V' to the dipole moment.

(iii) $s = 2$: When the case $\hat{A} = f\hat{p}^2$ is treated in exactly the same way as for $s = 1$ we find that

$$\epsilon_k'' = (\hbar^2/8m)\rho^{(4)} - \tfrac{1}{2} (\rho V')' ,$$

which is just the derivative of eq. (13) and therefore does not contain any new information.

(iv) $s = 3$: From

$$\langle\psi|[\hat{H}, f\hat{p}^3]|\psi\rangle = 0$$

it follows, analogously so the case $s = 1$, that

$$\frac{\hbar^2}{m} \int_a^b (f'\psi\psi^{(4)} + \tfrac{1}{2} f''\psi\psi''') \, \mathrm{d}x$$
$$+ \int_a^b f(3V'\psi\psi'' + 3V''\psi\psi' + V'''\psi^2) \, \mathrm{d}x = 0 , \tag{20}$$

or

$$\int_a^b f[-(\hbar^2/m)(\psi\psi^{(4)})' + (\hbar^2/2m)(\psi\psi''')''$$
$$+ 3V'\psi\psi'' + 3V''\psi\psi' + V'''\psi^2] \, \mathrm{d}x = 0 .$$

Again, from the arbitrariness of f it is deduced that the square bracket must vanish. Replacing ψ by ψ_i, summing over i and using

$$\frac{\partial^4 \rho(x,x')}{\partial x^2 \partial x'^2}\bigg|_{x'=x} = 2 \sum_{i=1}^{N/2} [\psi_i''(x)]^2 , \tag{21}$$

where

$$\rho(x,x') \equiv 2 \sum_{i=1}^{N/2} \psi_i(x)\psi_i(x') \tag{22}$$

is Dirac's density matrix, we obtain the "differential" relation

$$(\hbar^2/m)\, \partial^4\rho(x,x')/\partial x^2 \partial x'^2\big|_{x'=x}$$
$$= \tfrac{5}{2} \epsilon_k''(x) - (\hbar^2/4m)\, \rho^{(4)}(x) + \tfrac{3}{2} V'(x)\rho'(x)$$
$$- \frac{6m}{\hbar^2} \int_a^x V'\epsilon_k\, \mathrm{d}\xi + \int_a^x V'''\rho\, \mathrm{d}\xi . \tag{23}$$

From (20) we can derive a relation without the fourth order derivative of x, x'), however, at the price that this relation will be only integral, not pointwise as eq. (23). If we put $f = 1$ in eq. (20), the first two integrals give no contribution, and we find

$$\int_a^b V\epsilon_k' \, dx + \frac{\hbar^2}{6m} \int_a^b V''' \rho \, dx = 0 . \qquad (24)$$

ϵ_k' can be eliminated by eq. (13) so that we obtain

$$\int_a^b [VV' - (\hbar^2/12m) V'''] \rho \, dx = 0 . \qquad (25)$$

For $s \geqslant 4$ derivatives of the density matrix of at least fourth order will enter also the integral relations, so we will not go beyond $s = 3$.

3. Finally let us check whether the foregoing HVTs are satisfied by the expressions for ρ and ϵ_k as given in the most fundamental Thomas–Fermi (TF) approximation in the frame of density functional theory. In this approximation, for one dimension, eqs. (2), (3), and (21) are evaluated by using plane waves for ψ_i and by replacing the sum by an integral over wave number k from $-k_{TF}$ to $+k_{TF}$ where

$$k_{TF}(x) = [\alpha(\lambda - V(x))]^{1/2} \theta(\lambda - V(x)) \qquad (26)$$

($\alpha = \hbar^2/2m$; $\theta(u)$ is the unit step function; λ chemical potential). For ρ, ϵ_k we obtain [19]

$$\rho_{TF}(x) = (2/\pi) k_{TF}(x) , \qquad (27a)$$

$$\epsilon_{k,TF}(x) = \tfrac{1}{3} (\lambda - V) \rho_{TF} , \qquad (27b)$$

and

$$\partial^4 \rho_{TF}(x, x')/\partial x^2 \partial x'^2 |_{x'=x} = \tfrac{1}{5} k_{TF}^4 \rho_{TF} . \qquad (27c)$$

First of all it is clear that both the "differential" relations (15) and (23) cannot be satisfied in the TF-approximation since the second and fourth derivatives, respectively, of ρ_{TF} and hence of V cannot be cancelled. For instance, it turns out immediately that for $\lambda > V(x)$

$$\epsilon_{k,TF}(x) + \tfrac{1}{2} \int_a^x V'(\xi) \rho_{TF}(\xi) \, d\xi = 0 \neq (\hbar^2/8m) \rho_{TF}'''(x) , \qquad (28)$$

where a may be e.g. the smallest value with $\lambda = V(a)$. On the other hand, if we take b to be the largest value with $\lambda = V(b)$ then eq. (16) becomes

$$\int_a^b V' \rho_{TF} \, d\xi = -(4\alpha^{1/2}/3\pi)(\lambda - V(x))^{3/2}|_{x=a}^b = 0 , \quad (29)$$

and thus also the (integral) virial theorem (17) is obeyed as is well known for a long time [20].

Furthermore, integration by parts shows that

$$\int_a^b x^2 \epsilon_{k,TF} \, dx = \tfrac{1}{6} \int_a^b x^3 V' \rho_{TF} \, dx , \qquad (30)$$

and

$$\tfrac{2}{3} \int_a^b x^3 \epsilon_{k,TF} \, dx = \tfrac{1}{12} \int_a^b x^4 V' \rho_{TF} \, dx . \qquad (31)$$

Thus, theorem (18) is violated in any case, theorem (19) is violated unless the dipole moment vanishes, either by symmetry or by accident.

Finally, from (26), (27a, b) we find

$$\int_a^b V\epsilon_{k,TF}' \, dx = -\tfrac{1}{2} \int_a^b VV' \rho_{TF} \, dx$$

$$= (\alpha^{1/2}/\pi) [\tfrac{2}{3} \lambda(\lambda - V)^{3/2} - \tfrac{2}{5}(\lambda - V)^{5/2}]_{x=a}^b$$

$$= 0 . \qquad (32)$$

On the other hand, $\int_a^b V''' \rho_{TF} \, dx$ is, in general, not zero. E.g. the potential

$$V(x) \equiv c_1 x^2 + c_2 e^{c_3 x} \qquad (c_i > 0, i = 1, 2, 3) \qquad (33)$$

satisfies

$$\lim_{x \to \pm \infty} V(x) = +\infty , \qquad (34)$$

so that $V(x)$ has bound states for all λ. From

$$V'''(x) = c_2 c_3^3 e^{c_3 x} > 0 , \quad x \in \mathbb{R} \qquad (35)$$

it follows that

$$\int_a^b V''' \rho_{TF} \, dx > 0 , \qquad (36)$$

thus both the relations (24) and (25) are violated in TF-approximation.

In summary, only two of the HVTs given above are satisfied by $\rho_{TF}, \epsilon_{k,TF}$. Future work on HVTs should investigate

(i) to what extent other approximations (TFW etc.) violate the HVTs;

(ii) how to implement HVTs in density functional formalism (e.g. by use of Lagrange multipliers when solving the Euler equation of the minimization problem of the total energy functional) in order to improve densities;

(iii) relations in three-dimensional systems.

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