

## Local scaled Schrödinger relations and the virial theorem

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Local scaled Schrödinger relationships are derived connecting the potential (assumed homogeneous of degree  $q$ ) and the kinetic-energy operator and also between the total energy and the kinetic-energy operator. The virial relationships that follow from these local equations are derived. A reduced local energy connection between the total energy and the kinetic-energy operator is derived in terms of "scaled one- and two-particle density matrices."

### I. INTRODUCTION

One necessary constraint that a wave function represent an accurate solution of the Schrödinger equation is that the virial theorem be satisfied, and this is achieved by making a scale transformation of the coordinates of the approximate wave function. Various aspects of this problem and other details on the virial theorem have been discussed at length in the literature.<sup>1-3</sup>

It is possible to derive simple local connections in configuration space between the kinetic-energy operator, the potential-energy operator and the total energy simply by making scale transformations of all coordinates in configuration space for the exact eigenfunction and the Hamiltonian operator. The principal restriction employed is that the potential operator be homogeneous of some specified degree. Potentials which can be decomposed into a sum of terms which are homogeneous of different degrees can also be employed, though the resulting expressions rapidly become complicated for this situation.

The local relationships between the kinetic-energy operator, the potential operator, and the total energy that are derived in this note have obvious similarity with the virial relationships. However, the former are best regarded simply as scaled relations, since virial connections involve some averaging procedure; in classical mechanics a time average of the kinetic energy, in quantum mechanics a spatial average of the kinetic and potential operators is employed.

### II. SCALED RELATIONS

The starting point for the derivation of local scaled Schrödinger relations is the Schrödinger equation

$$H(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (1)$$

To simplify notation,  $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is denoted by

$\vec{r}$ . It is assumed that the Hamiltonian can be written as

$$H(\vec{r}) = T(\vec{r}) + V(\vec{r}), \quad (2)$$

where  $T(\vec{r})$  is the kinetic energy operator and  $V(\vec{r})$  is the potential operator which will be taken to be homogeneous of degree  $q$ .

If each coordinate in Eq. (1) is multiplied by the scale factor  $\lambda_i$ , then

$$[T(\lambda_i \vec{r}) + V(\lambda_i \vec{r})]\Psi(\lambda_i \vec{r}) = E\Psi(\lambda_i \vec{r}), \quad (3)$$

and similarly for a different scale factor  $\lambda_j$  ( $\lambda_i \neq \lambda_j$ )

$$[T(\lambda_j \vec{r}) + V(\lambda_j \vec{r})]\Psi(\lambda_j \vec{r}) = E\Psi(\lambda_j \vec{r}). \quad (4)$$

The kinetic-energy operator satisfies

$$T(\lambda_i \vec{r}) = \lambda_i^{-2}T(\vec{r}). \quad (5)$$

Substituting Eq. (5) into Eqs. (3) and (4) leads to

$$\begin{aligned} \lambda_i^{-2}\Psi(\lambda_j \vec{r})T(\vec{r})\Psi(\lambda_i \vec{r}) - \lambda_j^{-2}\Psi(\lambda_i \vec{r})T(\vec{r})\Psi(\lambda_j \vec{r}) \\ = \Psi(\lambda_i \vec{r})\Psi(\lambda_j \vec{r})[V(\lambda_j \vec{r}) - V(\lambda_i \vec{r})], \end{aligned} \quad (6)$$

and we have assumed that  $V(\vec{r})$  contains no differential operator. If the homogeneous assumption for  $V(\vec{r})$  is employed, then

$$V(\lambda_i \vec{r}) = \lambda_i^q V(\vec{r}). \quad (7)$$

Using Eq. (7), Eq. (6) simplifies to give

$$\begin{aligned} V(\vec{r}) = [(\lambda_i^q - \lambda_j^q)\Psi(\lambda_i \vec{r})\Psi(\lambda_j \vec{r})]^{-1} \\ \times [\lambda_i^{-2}\Psi(\lambda_j \vec{r})T(\vec{r})\Psi(\lambda_i \vec{r}) \\ - \lambda_j^{-2}\Psi(\lambda_i \vec{r})T(\vec{r})\Psi(\lambda_j \vec{r})]. \end{aligned} \quad (8)$$

Equation (8) constitutes a local scaled connection between the potential- and kinetic-energy operator and the wave function. The special case of Eq. (8) of most significance in molecular quantum mechanics is when  $V(\vec{r})$  represents the Coulomb potential, and so  $q = -1$ . For this case Eq. (8) reads

$$\begin{aligned} V(\vec{r}) = (\lambda_i - \lambda_j)[\lambda_i^3\lambda_j^3\Psi(\lambda_i \vec{r})\Psi(\lambda_j \vec{r})]^{-1} \\ \times [\lambda_j^2\Psi(\lambda_j \vec{r})T(\vec{r})\Psi(\lambda_i \vec{r}) \\ - \lambda_i^2\Psi(\lambda_i \vec{r})T(\vec{r})\Psi(\lambda_j \vec{r})]. \end{aligned} \quad (9)$$

Instead of eliminating the energy from Eqs. (3) and (4), the potential operator may instead be eliminated to determine a local relationship connecting  $E$  and  $T$ . From Eqs. (3) and (4) we obtain

$$E\Psi(\lambda_i\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}}) = \frac{\lambda_j^{2+q}\Psi(\lambda_j\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_i\bar{\mathbf{r}}) - \lambda_i^{2+q}\Psi(\lambda_i\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}})}{\lambda_i^2\lambda_j^2(\lambda_j^q - \lambda_i^q)}, \quad (10)$$

which simplifies for the special case of a Coulomb potential ( $q = -1$ ) to give

$$E\Psi(\lambda_i\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}}) = \frac{\lambda_j\Psi(\lambda_j\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_i\bar{\mathbf{r}}) - \lambda_i\Psi(\lambda_i\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}})}{\lambda_i\lambda_j(\lambda_i - \lambda_j)}. \quad (11)$$

Equation (10) represents a generalization of a relation given recently by Levy.<sup>4</sup>

If a third scale parameter  $\lambda_k$  ( $\lambda_k \neq \lambda_i$ ;  $\lambda_k \neq \lambda_j$ ) is introduced, both the potential operator and the energy can be eliminated to obtain a local constraint involving the wave function for the three different scales and the kinetic-energy operator; that is,

$$\begin{aligned} &(\lambda_i^q - \lambda_j^q)\lambda_i^2\lambda_j^2\Psi(\lambda_i\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_k\bar{\mathbf{r}}) \\ &+ (\lambda_j^q - \lambda_k^q)\lambda_j^2\lambda_k^2\Psi(\lambda_j\bar{\mathbf{r}})\Psi(\lambda_k\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_i\bar{\mathbf{r}}) \\ &+ (\lambda_k^q - \lambda_i^q)\lambda_k^2\lambda_i^2\Psi(\lambda_k\bar{\mathbf{r}})\Psi(\lambda_i\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}}) = 0, \quad (12) \end{aligned}$$

which may be written in compact form as

$$P_{ijk}[(\lambda_i^q - \lambda_j^q)\lambda_i^2\lambda_j^2\Psi(\lambda_i\bar{\mathbf{r}})\Psi(\lambda_j\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_k\bar{\mathbf{r}})] = 0, \quad (13)$$

where  $P_{ijk}$  denotes the sum of the terms with the indices  $ijk$  permuted in a cyclic manner. Equation (13) represents a *necessary* criterion which the exact wave function must satisfy. The case of particular interest is that of the Coulomb potential ( $q = -1$ ); so that Eq. (13) becomes

$$P_{ijk}[(\lambda_i - \lambda_j)\lambda_i\lambda_j\Psi(\lambda_j\bar{\mathbf{r}})\Psi(\lambda_i\bar{\mathbf{r}})T(\bar{\mathbf{r}})\Psi(\lambda_k\bar{\mathbf{r}})] = 0. \quad (14)$$

Equation (11) exhibits a local dependence on the set of all coordinates  $\{\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \dots, \bar{\mathbf{r}}_N\}$ . This equation may be reduced to a relationship depending locally on only a single-electron coordinate by integration over all coordinates but one. From Eq. (11) we have

$$\begin{aligned} &(\lambda_i - \lambda_j)\lambda_i\lambda_j E \int \Psi(\lambda_i\bar{\mathbf{r}}_1, \dots, \lambda_i\bar{\mathbf{r}}_N)\Psi(\lambda_j\bar{\mathbf{r}}_1, \dots, \lambda_j\bar{\mathbf{r}}_N)d\bar{\mathbf{r}}_2 \dots d\bar{\mathbf{r}}_N \\ &= \int [\lambda_j\Psi(\lambda_j\bar{\mathbf{r}}_1, \dots, \lambda_j\bar{\mathbf{r}}_N)T(\bar{\mathbf{r}}_1, \dots, \bar{\mathbf{r}}_N)\Psi(\lambda_i\bar{\mathbf{r}}_1, \dots, \lambda_i\bar{\mathbf{r}}_N) \\ &\quad - \lambda_i\Psi(\lambda_i\bar{\mathbf{r}}_1, \dots, \lambda_i\bar{\mathbf{r}}_N)T(\bar{\mathbf{r}}_1, \dots, \bar{\mathbf{r}}_N)\Psi(\lambda_j\bar{\mathbf{r}}_1, \dots, \lambda_j\bar{\mathbf{r}}_N)]d\bar{\mathbf{r}}_2 \dots d\bar{\mathbf{r}}_N, \quad (15) \end{aligned}$$

which can be simplified to

$$\begin{aligned} &(\lambda_i - \lambda_j)\lambda_i\lambda_j E \rho_1(\lambda_i\bar{\mathbf{r}}_1; \lambda_j\bar{\mathbf{r}}_1) = \left( T(\bar{\mathbf{r}}_1)[\lambda_j\rho_1(\lambda_i\bar{\mathbf{r}}_1; \lambda_j\bar{\mathbf{r}}_1') - \lambda_i\rho_1(\lambda_j\bar{\mathbf{r}}_1; \lambda_i\bar{\mathbf{r}}_1')] \right. \\ &\quad \left. + \int_{2'=2} [\lambda_j T(\bar{\mathbf{r}}_2)\rho_2(\lambda_i\bar{\mathbf{r}}_1, \lambda_i\bar{\mathbf{r}}_2; \lambda_j\bar{\mathbf{r}}_1', \lambda_j\bar{\mathbf{r}}_2') \right. \\ &\quad \left. - \lambda_i T(\bar{\mathbf{r}}_2)\rho_2(\lambda_j\bar{\mathbf{r}}_1, \lambda_j\bar{\mathbf{r}}_2; \lambda_i\bar{\mathbf{r}}_1', \lambda_i\bar{\mathbf{r}}_2')]d\bar{\mathbf{r}}_2 \right)_{1'=1}, \quad (16) \end{aligned}$$

where the "scaled one- and two-particle density matrices," with scale parameters  $\lambda_i$  and  $\lambda_j$  are given, respectively, by

$$\rho_1(\lambda_i\bar{\mathbf{r}}_1; \lambda_j\bar{\mathbf{r}}_1') = N \int \Psi(\lambda_i\bar{\mathbf{r}}_1, \dots, \lambda_i\bar{\mathbf{r}}_N)\Psi(\lambda_j\bar{\mathbf{r}}_1', \lambda_j\bar{\mathbf{r}}_2, \dots, \lambda_j\bar{\mathbf{r}}_N)d\bar{\mathbf{r}}_2 \dots d\bar{\mathbf{r}}_N, \quad (17)$$

$$\rho_2(\lambda_i\bar{\mathbf{r}}_1, \lambda_i\bar{\mathbf{r}}_2; \lambda_j\bar{\mathbf{r}}_1', \lambda_j\bar{\mathbf{r}}_2') = N(N-1) \int \Psi(\lambda_i\bar{\mathbf{r}}_1, \dots, \lambda_i\bar{\mathbf{r}}_N)\Psi(\lambda_j\bar{\mathbf{r}}_1', \lambda_j\bar{\mathbf{r}}_2', \lambda_j\bar{\mathbf{r}}_3, \dots, \lambda_j\bar{\mathbf{r}}_N)d\bar{\mathbf{r}}_3 \dots d\bar{\mathbf{r}}_N. \quad (18)$$

In the limit  $\lambda_i \rightarrow 1$  and  $\lambda_j \rightarrow 1$ , Eqs. (17) and (18) reduce to the normal definitions (for real eigenfunctions) of the one- and two-particle density matrices, respectively. With the notational simplifications

$$\rho_{1\lambda_i\lambda_j} \equiv \rho_1(\lambda_i\bar{\mathbf{r}}_1; \lambda_j\bar{\mathbf{r}}_1'), \quad (19)$$

$$\rho_{1d\lambda_i\lambda_j} \equiv \rho_1(\lambda_i\bar{\mathbf{r}}_1; \lambda_j\bar{\mathbf{r}}_1), \quad (20)$$

$$\rho_{2\lambda_i\lambda_j} \equiv \rho_2(\lambda_i\bar{\mathbf{r}}_1, \lambda_i\bar{\mathbf{r}}_2; \lambda_j\bar{\mathbf{r}}_1', \lambda_j\bar{\mathbf{r}}_2'). \quad (21)$$

Equation (16) may be written as

$$E_{\rho_{1d\lambda_i\lambda_j}} = P_{ij} \left[ \left( T(\mathbf{r}_1) \rho_{1\lambda_i\lambda_j} + \int_{2'=2} T(\mathbf{r}_2) \rho_{2\lambda_i\lambda_j} d\mathbf{r}_2 \right) / \lambda_i(\lambda_i - \lambda_j) \right]_{1'=1}, \quad (22)$$

which is the reduced local scaled relationship between the energy and kinetic-energy operator in "density matrix" form.

### III. VIRIAL CONNECTIONS

Generalized virial relationships may be derived directly by integrating the appropriate equations of the previous section over all configuration coordinates. From Eq. (8)

$$\begin{aligned} (\lambda_j^q - \lambda_i^q) \langle \Psi(\lambda_i \mathbf{r}) | V(\mathbf{r}) | \Psi(\lambda_j \mathbf{r}) \rangle \\ = \lambda_i^{-2} \langle \Psi(\lambda_j \mathbf{r}) | T | \Psi(\lambda_i \mathbf{r}) \rangle - \lambda_j^{-2} \langle \Psi(\lambda_i \mathbf{r}) | T | \Psi(\lambda_j \mathbf{r}) \rangle, \end{aligned} \quad (23)$$

that is,

$$\frac{\langle \Psi(\lambda_i \mathbf{r}) | T | \Psi(\lambda_j \mathbf{r}) \rangle}{\langle \Psi(\lambda_i \mathbf{r}) | V | \Psi(\lambda_j \mathbf{r}) \rangle} = \frac{\lambda_i^2 \lambda_j^2 (\lambda_j^q - \lambda_i^q)}{(\lambda_j^2 - \lambda_i^2)}. \quad (24)$$

For the special case  $q = -1$ , Eq. (24) simplifies to

$$\frac{\langle \Psi(\lambda_i \mathbf{r}) | T | \Psi(\lambda_j \mathbf{r}) \rangle}{\langle \Psi(\lambda_i \mathbf{r}) | V | \Psi(\lambda_j \mathbf{r}) \rangle} = -\lambda_i \lambda_j (\lambda_i + \lambda_j)^{-1}. \quad (25)$$

For the particular case  $\lambda_i = 1$  and  $\lambda_j \rightarrow 1$ , Eq. (25) yields

$$\frac{\langle \Psi(\mathbf{r}) | T | \Psi(\mathbf{r}) \rangle}{\langle \Psi(\mathbf{r}) | V | \Psi(\mathbf{r}) \rangle} = -\frac{1}{2}, \quad (26)$$

which is the usual virial relation connecting matrix elements of  $T$  and  $V$ . Note that although Eq. (25) is defined for  $\lambda_i = \lambda_j = 1$ , the starting equation (8) assumes  $\lambda_i \neq \lambda_j$ .

In a similar manner, we have from Eq. (10)

$$E = \frac{(\lambda_j^{2+q} - \lambda_i^{2+q}) \langle \Psi(\lambda_i \mathbf{r}) | T | \Psi(\lambda_j \mathbf{r}) \rangle}{\lambda_i^2 \lambda_j^2 (\lambda_j^q - \lambda_i^q) \langle \Psi(\lambda_i \mathbf{r}) | \Psi(\lambda_j \mathbf{r}) \rangle}. \quad (27)$$

For the special case  $q = -1$ , Eq. (27) simplifies to

$$E = -\frac{\langle \Psi(\lambda_i \mathbf{r}) | T | \Psi(\lambda_j \mathbf{r}) \rangle}{\lambda_i \lambda_j \langle \Psi(\lambda_i \mathbf{r}) | \Psi(\lambda_j \mathbf{r}) \rangle}. \quad (28)$$

Taking  $\lambda_i = 1$  and the limit  $\lambda_j \rightarrow 1$  in Eq. (28) gives

$$E = -\langle \Psi | T | \Psi \rangle. \quad (29)$$

A simple local connection between  $E$  and  $V$  is not available, since  $\Psi(\lambda \mathbf{r})$  cannot be expressed as a simple product of a scale factor multiplied by  $\Psi(\mathbf{r})$ . The connection between the total energy and matrix elements of  $V$  can be obtained from Eqs. (24) and (27), and the result is

$$E = \frac{(\lambda_j^{2+q} - \lambda_i^{2+q}) \langle \Psi(\lambda_i \mathbf{r}) | V | \Psi(\lambda_j \mathbf{r}) \rangle}{(\lambda_j^2 - \lambda_i^2) \langle \Psi(\lambda_i \mathbf{r}) | \Psi(\lambda_j \mathbf{r}) \rangle}, \quad (30)$$

which simplifies for the special case  $q = -1$  to give

$$E = (\lambda_i + \lambda_j)^{-1} \frac{\langle \Psi(\lambda_i \mathbf{r}) | V | \Psi(\lambda_j \mathbf{r}) \rangle}{\langle \Psi(\lambda_i \mathbf{r}) | \Psi(\lambda_j \mathbf{r}) \rangle}. \quad (31)$$

Setting  $\lambda_i = 1$  and  $\lambda_j \rightarrow 1$ , gives the well-known virial relation

$$E = \frac{1}{2} \langle \Psi | V | \Psi \rangle. \quad (32)$$

In summary, local scaled Schrödinger relations represent *necessary* conditions which the exact wave function (corresponding to a particular potential) must satisfy. Such relationships represent more severe restrictions of the wave function than the standard virial conditions. The usual virial relations, which have been widely employed in molecular quantum mechanics, test the wave function quality in the global sense. However, local scaled Schrödinger relations can be used to test the quality of the wave function at any point in configuration space. For this reason the local scaled Schrödinger relations should be of some significance in molecular quantum mechanics.

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