

## A naive look on the Hohenberg–Kohn theorem

K.D. Sen<sup>a</sup>, Emili Besalú<sup>b</sup> and Ramon Carbó-Dorca<sup>b</sup>

<sup>a</sup> School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

<sup>b</sup> Institute of Computational Chemistry, University of Girona, Girona 17071, Catalonia, Spain

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A generalised Hohenberg–Kohn theorem is described in terms of the sign of the second-order energy variation. Independently, it is also corroborated within the perturbation theoretical framework. An alternative formulation of the Hohenberg–Kohn theorem, based on the relationships involving the matrix representations of density functions and the Hamiltonian operator variations, is shown to extend the validity of the theorem to the excited states of the Hamiltonian operators possessing non-degenerate spectra. Finally, a connection with Brillouin's theorem when energy variation becomes stationary is also outlined.

### 1. Introduction

Recently, Mezey [11] has arrived at the Hohenberg–Kohn theorem (HKT) [8], using an information theoretical approach and has also derived a new theorem on density functions – the holographic electron density theorem. This work [11] has motivated us to attempt at the generalisation of the HKT and examine its consequences.

### 2. Generalised Hohenberg–Kohn theorem

Consider a quantum system, with an attached Hamiltonian  $H_0$ , with a non-degenerate ground state characterised by the energy–wavefunction pair  $\{E_0, \Psi_0\}$ , and another system with known Hamiltonian  $H$ , with a non-degenerate ground state described by the pair  $\{E, \Psi\}$ . Assuming that both wavefunctions are normalised, then the following relationships will hold:  $E_0 = \langle \Phi_0 | H_0 | \Psi_0 \rangle$  and  $E = \langle \Psi | H | \Psi \rangle$ . Also, approximate energies for both ground states can be defined, by exchanging the positions of both wavefunctions, respectively, as  $E_{a,0} = \langle \Psi | H_0 | \Psi \rangle$  and  $E_a = \langle \Psi_0 | H | \Psi_0 \rangle$ . In general, and independently of the system description, the inequalities  $\Delta_0 = E_0 - E_{a,0} \leq 0$  and  $\Delta = E - E_a \leq 0$  will be valid.

Formally, from both wavefunctions, arbitrary order density functions can be build up [3,4,9,10]. Here, the process of constructing density functions of arbitrary order will be symbolised, for both the ground states considered above, by the projectors  $\rho_0 = |\Psi_0\rangle\langle\Psi_0|$  and  $\rho = |\Psi\rangle\langle\Psi|$ , respectively, Owing to this last convention, another set of energy expressions can be used, namely,  $E_0 = \langle H_0 | \rho_0 \rangle$  and  $E = \langle H | \rho \rangle$ . This

can be extended to approximate energy expressions as well, that is,  $E_{a;0} = \langle H_0 | \rho \rangle$  and  $E_a = \langle H | \rho_0 \rangle$ . Such an expectation value formalism was previously used to establish the theoretical background of the so-called structure–property or structure–activity relationships [1,5,6]. A detailed mathematical analysis will be published elsewhere.

The negative energy difference, previously defined for the first system, can be formally rewritten now as follows:  $\Delta_0 = \langle H_0 | \rho_0 \rangle - \langle H_0 | \rho \rangle = \langle H_0 | \rho_0 - \rho \rangle = \langle H_0 | \Delta \rho \rangle$ , and a similar sequence can be written for the second system:  $\Delta = \langle H | \rho \rangle - \langle H | \rho_0 \rangle = -\langle H | \rho_0 - \rho \rangle = -\langle H | \Delta \rho \rangle$ .

Since both energy differences are non-positive definite, the following inequality holds rigorously:  $\Delta_0 + \Delta \leq 0$ . This will give rise to the following sequence of differences:  $\Delta_0 + \Delta = \langle H_0 | \Delta \rho \rangle - \langle H | \Delta \rho \rangle = \langle H_0 - H | \Delta \rho \rangle = \langle \Delta H | \Delta \rho \rangle \leq 0$ .

The last inequality above shows that the action of the Hamiltonian increment upon the density difference will be, in any case, a non-positive definite quantity, which can be symbolised by the expression  $\langle \Delta H | \Delta \rho \rangle \leq 0$ . Four cases can be considered, which arise out of the respective increments being null or not. But only the diagonal situations, the ones with both increments simultaneously null or not null, will be relevant. Precisely, the situation  $\Delta H \neq 0$  and  $\Delta \rho = 0$  produces the *reductio ad absurdum*, and was used [8] to deduce the HKT, as the argument to accept the functional interdependence of density and potential. The similar and equally non-realistic increment values,  $\Delta H = 0$  and  $\Delta \rho \neq 0$ , can also be discarded. The couple of remaining possibilities provide the trivial equality  $\langle \Delta H | \Delta \rho \rangle = 0$  when both increments are null; and, finally, when  $\Delta H \neq 0$  and  $\Delta \rho \neq 0$ , the result  $\langle \Delta H | \Delta \rho \rangle < 0$  will hold. Alternatively, under special conditions, this final case could also produce  $\langle \Delta H | \Delta \rho \rangle = 0$ . This can be understood by considering  $\langle \Delta H | \Delta \rho \rangle$  as a formal scalar product within the space containing both operator increments. Then, even if both the implied operator differences are non-null, the condition that  $\Delta H \perp \Delta \rho$  would imply a null product.

### 3. Second-order energy variation and perturbation

So far, and according to the last remarks, the resultant inequality,  $\langle \Delta H | \Delta \rho \rangle \leq 0$ , can be considered a generalised HKT (GHKT). But, continuing the analysis of such an inequality, suppose that the increments transform into variations, then  $\langle \delta H | \delta \rho \rangle \leq 0$  must hold. This last variational inequality suggests that *on performing first-order variations over both the Hamiltonian and the density function, the resulting second-order energy variation part will always be negative or null*.

It is easy to see that the variational form of the GHKT corresponds to the fact that the second-order ground state energy variation will be non-positive definite. The argument is almost trivial. According to the previous description, the energy can be formally written as  $E = \langle H | \rho \rangle$ . Suppose a first-order variation is done on both the Hamiltonian and the density function, that is,  $H \rightarrow H + \delta H$  and  $\rho \rightarrow \rho + \delta \rho$ , then the ground state energy variation could be written, up to second order, in the simple form  $\delta E = \langle \delta H | \rho \rangle + \langle H | \delta \rho \rangle + \langle \delta H | \delta \rho \rangle$ . The GHKT developed here states that the third term, constituting a second-order variation, is negative or null.

The result obtained above using simple bra–ket algebra will be now deduced following the well-known Rayleigh–Schrödinger perturbation theory (RS PT). It can be shown in general that second-order RS PT corrections to a non-degenerate ground state energy are non-positive definite. It will be instructive to give schematic arguments to prove this. Take the initial Hamiltonians, and suppose the classical first-order perturbation into the Hamiltonian relates both operators:  $H = H_0 + \lambda H_1$ , where  $\lambda$  is the perturbation parameter. Consider also that, in fact, the perturbation operator can be associated with the previously used Hamiltonian variation, that is,  $H_1 \equiv \delta H$ .

Then, textbook procedures, see for example [7,12], can easily show that second-order corrections to the non-degenerate ground state energies can be given, following the well-known expression

$$E_{2,0} = \sum_{\forall k > 0} (E_{0,0} - E_{0,k})^{-1} |\langle k; 0 | \delta H | 0; 0 \rangle|^2,$$

where  $E_{n,k}$  stands for the  $n$ th-order energy correction for the  $k$ th state, that is,  $E_{0,0}$  is the unperturbed ground state energy; while  $E_{0,k}$  ( $\forall k > 0$ ) stand for the unperturbed excited states energies. The same indices have been used to indicate the wavefunctions. The symbols  $|n; k\rangle$  represent the  $n$ th corrections to the  $k$ th state, and  $n = 0$  will give rise to the orthonormalised unperturbed wavefunction set.

Observing the above expression for the second-order correction to ground state energy,  $E_{2,0}$ , one can see that the sign of the expression will only depend on the sign of the energy differences between the ground state and the whole set of excited state energies:  $\Delta_{0k} = E_{0,0} - E_{0,k}$ ; it is easy to see that  $\Delta_{0k} < 0$  ( $\forall k > 0$ ). As in the GHKT, it is obtained through RS PT reasoning that necessarily  $E_{2,0} \leq 0$ . The equality will be fulfilled when  $\delta H = 0$ . Note that in this argumentation the perturbation operator  $\delta H = H - H_0$  has the sign changed with respect to the previously used Hamiltonian increment, but as the Hamiltonian perturbation appears within a squared module, this feature is irrelevant here.

#### 4. First-order density variation: A reformulation of HKT

Using the intermediate results, leading to the second-order correction to the energy, the first-order correction to the ground state density can be easily deduced. From the well-known expression of the first-order correction to the ground state wavefunction, expressed using the same conventions as before, the following equality is obtained:

$$|1; 0\rangle = \sum_{\forall k > 0} (\Delta_{0k})^{-1} P_{0;k} \delta H |0; 0\rangle,$$

where the projector over the  $k$ th excited state is symbolised by  $P_{0;k} = |0; k\rangle\langle k; 0|$ . Besides, the variation of the unperturbed ground state wavefunction can be computed as the corresponding first-order correction:  $\delta|0; 0\rangle \equiv |1; 0\rangle$ .

Thus, it is easy to deduce that first-order variation into the density function,  $\delta\rho_0$ , can be expressed as

$$\delta\rho_0 = \sum_{\forall k > 0} (\Delta_{0k})^{-1} (P_{0;k} \delta H P_{0;0} + P_{0;0} \delta H P_{0;k}),$$

where the symbol  $P_{0;0} = |0;0\rangle\langle 0;0|$  has been used as the projector over the ground state wavefunction.

Projecting  $\delta\rho_0$  over an excited state  $|0;r\rangle$  on the left and over the ground state on the right produces  $P_{0;r} \delta\rho_0 P_{0;0} = (\Delta_{0r})^{-1} P_{0;r} \delta H P_{0;0}$ . Rearranging terms, owing to the projector expressions, the following relationship, relating the variation of density and Hamiltonian, is found:  $\langle r;0 | \delta\rho_0 | 0;0 \rangle | 0;r \rangle \langle 0;0| = (\Delta_{0r})^{-1} \langle r;0 | \delta H | 0;0 \rangle | 0;r \rangle \langle 0;0|$ .

A similar complex conjugate expression holds when reversing the projector sides of the first-order density variation. It can be deduced, then, that there are two equalities relating both operator representations, namely,  $\langle r;0 | \delta\rho_0 | 0;0 \rangle = (\Delta_{0r})^{-1} \langle r;0 | \delta H | 0;0 \rangle$ , and its complex conjugate. This last result can be interpreted in the sense that the matrix representation components of the ground state density and Hamiltonian operator first-order variations differ only in a scalar negative constant. Thus, *Hamiltonian variation representations can be substituted by ground state density variation representations, and vice versa. This constitutes another formulation of the HKT.*

*Mutatis mutandis*,  $\delta\rho_p$ , the density variation for some  $p$ th excited state  $|0;p\rangle$  can be expressed using perturbation theory in the same way as in the ground state discussion above. Provided that the unperturbed Hamiltonian is characterised by a non-degenerate spectrum, the difference will consist in that the ground state function must be replaced by the corresponding excited state one:  $|0;0\rangle \rightarrow |0;p\rangle$ , and state energy differences be changed accordingly:  $\Delta_{0k} \rightarrow \Delta_{pk}$ .

The  $p$ th excited state HKT alternative formulation, after projection of the  $\delta\rho_p$  expression on the left by  $P_{0;r}$  and on the right by  $P_{0;p}$ , will correspond to the equalities  $\langle r;0 | \delta\rho_p | 0;p \rangle = (\Delta_{pr})^{-1} \langle r;0 | \delta H | 0;p \rangle$ , accompanied by the complex conjugate, which will be obtained when changing the projectors' sides. Comparison with ground state results indicates that the sign of the difference set  $\{\Delta_{pr}\}$  cannot remain uniquely negative, when excited states are considered. *Such relationships will extend the validity of the HKT to the excited states as well.*

## 5. Final remarks

An equivalent situation, affecting the ground state, can be obtained if it is taken into account that as the RS PT result,  $E_{2;0} \leq 0$ , is independent of the sign of  $\delta H$ , then *GHKT*,  $\langle \delta H | \delta\rho_0 \rangle \leq 0$ , implies  $\text{sign}(\delta\rho_0) = -\text{sign}(\delta H)$ , corroborating the interconnection between these variation representations found previously using RS PT. This relationship is made obvious when analysing the structure of  $\delta\rho_0$  given above.

Also, using again the RS PT expression for  $\delta\rho_0$ , and realising that the pairs  $\{E(0;k), |0;k\rangle\}$  ( $\forall k$ ) are orthonormalised eigenstates of the unperturbed Hamiltonian,

it is easy to prove that  $\langle H_0 | \delta \rho_0 \rangle = 0$ . Thus, the ground state energy variation can be written with a unique first-order term:  $\delta E_0 = \langle \delta H | \rho_0 \rangle + \langle \delta H | \delta \rho_0 \rangle \equiv E_{1;0} + E_{2;0}$ . Moreover, at the stationary state,  $\delta E_0 = 0$ , and thus  $\langle \delta H | \rho_0 \rangle = -\langle \delta H | \delta \rho_0 \rangle$ . This is the same as saying that when ground state energy optimum is reached,  $\langle \delta H | \rho_0 \rangle = \langle \delta H \rangle \geq 0$ . *The expectation value of the Hamiltonian variation at the ground stationary state neighbourhood will be non-negative definite.* This result can be connected with Brillouin's theorem [2].

## 6. Conclusions

Standard quantum chemical arguments have been used to generalise and reformulate the Hohenberg–Kohn theorem with possible extension of the theorem to include the excited states. A connection with Brillouin's theorem is also discussed.

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