The Virial and Hellmann-Feynman Theorems

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This chapter discusses two theorems that aid in understanding chemical bonding: the *virial* theorem and the *Hellmann-Feynman* theorem, which are here presented after a preliminary introduction illustrating another theorem of quantum mechanics due to Eherenfest.
The Eherenfest Theorem

The Eherenfest theorem deals with the expectation values of the position and momentum operators of a particle of mass $m$ and the expectation value of the force acting on it. In particular it relates the time derivative of $\langle r \rangle$ to $\langle p \rangle$ and the time derivative of $\langle p \rangle$ to $\langle F \rangle$, where $F = -\nabla V$, i.e., the gradient of the scalar potential in which the particle moves. The theorem states

$$\frac{d}{dt} \langle r_x \rangle = \frac{1}{m} \langle p_x \rangle$$

$$\frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle$$
Eherenfest’s theorem can be proved to be a special case of a more general relation of quantum mechanics, which connects the time derivative of the expectation value of any quantum mechanical operator $\hat{A}$ to the commutator of that operator and the Hamiltonian of the system

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle + \langle \frac{\partial A}{\partial t} \rangle$$

If the operator $\hat{A}$ does not contain time explicitly the last term in the above equation will be vanishing.
Let us derive the above equation within the Schrödinger picture, i.e., \( i\hbar(\partial\Phi/\partial t) = \hat{H}\Phi \)

\[
\frac{d}{dt} \langle A \rangle = \frac{d}{dt} \left\langle \Phi \left| \hat{A} \right| \Phi \right\rangle \\
= \left\langle \left( \frac{\partial\Phi}{\partial t} \right) \left| \hat{A} \right| \Phi \right\rangle + \left\langle \Phi \left| \left( \frac{\partial\hat{A}}{\partial t} \right) \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{A} \left( \frac{\partial\Phi}{\partial t} \right) \right| \Phi \right\rangle \\
= \left\langle \left( \frac{\hat{H}\Phi}{i\hbar} \right) \left| \hat{A} \right| \Phi \right\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle + \left\langle \Phi \left| \hat{A} \left( \frac{\hat{H}\Phi}{i\hbar} \right) \right| \Phi \right\rangle \\
= \frac{1}{i\hbar} \left( \left\langle \Phi \left| \hat{A} \right| \hat{H}\Phi \right\rangle - \left\langle \hat{H}\Phi \left| \hat{A} \right| \Phi \right\rangle \right) + \left\langle \frac{\partial A}{\partial t} \right\rangle \\
= \frac{1}{i\hbar} \left\langle \Phi \left| \hat{A}\hat{H} - \hat{H}\hat{A} \right| \Phi \right\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle \\
= \frac{1}{i\hbar} \left\langle [\hat{A}, \hat{H}] \right\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle \quad \text{C.V.D.}
\]
Setting $\hat{A} = r_x$ one has

$$\frac{d}{dt} \langle r_x \rangle = \frac{1}{i\hbar} \langle [r_x, \hat{H}] \rangle$$

Using $[r_x, \hat{H}] = \frac{i\hbar}{m} p_x$, see Levine Quantum Chemistry (5.9)

$$\frac{d}{dt} \langle r_x \rangle = \frac{1}{m} \langle p_x \rangle$$
Setting \( \hat{A} = p_x \) one has

\[
\frac{d}{dt} \langle p_x \rangle = \frac{1}{i\hbar} \langle [p_x, \hat{H}] \rangle
\]

Considering that

\[
[p_x, \hat{H}] = [p_x, \hat{T}] + [p_x, \hat{V}] = [p_x, \hat{V}] = -i\hbar[\nabla_x, V]
\]

\[
= -i\hbar (\nabla_x V \cdot + V \cdot \nabla_x - V \cdot \nabla_x) = -i\hbar \frac{\partial V}{\partial x}
\]

Therefore

\[
\frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle
\]

and Ehrenfest’s theorem is proved.
The Hypervirial Theorem

Let $\psi_n$ and $\psi_m$ be two bound stationary states of a system

$$\hat{H}\psi_n = E_n\psi_n \quad , \quad \hat{H}\psi_m = E_m\psi_m$$

Let $\hat{A}$ be a linear, time-independent operator. Consider the integral

$$\int \psi_n^* \left[ \hat{H}, \hat{A} \right] \psi_m \, d\tau = \langle n \left| \hat{H}\hat{A} - \hat{A}\hat{H} \right| m \rangle = \langle n \left| \hat{H}\hat{A} \right| m \rangle - \langle n \left| \hat{A}\hat{H} \right| m \rangle$$

Since $\hat{H}$ is hermitian, the following hypervirial identities are obtained

$$\int \psi_n^* \left[ \hat{H}, \hat{A} \right] \psi_m \, d\tau = (E_n - E_m) \langle n \left| \hat{A} \right| m \rangle$$

$$\int \psi_n^* \left[ \hat{H}, \hat{A} \right] \psi_n \, d\tau = 0$$
Considering that

\[
[\hat{H}, r_x] = -\frac{i\hbar}{m} p_x
\]

\[
[\hat{H}, p_x] = i\hbar \frac{\partial V}{\partial x}
\]

one obtains

\[
\langle n | r_x | m \rangle = -\frac{i\hbar}{m} \frac{\langle n | p_x | m \rangle}{E_n - E_m}
\]

\[
\langle n | p_x | m \rangle = i\hbar \frac{\langle n | \frac{\partial V}{\partial x} | m \rangle}{E_n - E_m}
\]

which can be used to switch between the so called length, velocity and force formalisms.
We now derive the **virial theorem** for a system containing $n$ particles from the hypervirial relation

$$\int \psi_n^* \left[ \hat{H}, \hat{A} \right] \psi_n \ d\tau = 0$$

We choose $\hat{A}$ to be

$$\sum_i^{n} \hat{r}_{\alpha i} \hat{p}_{\alpha i} = -i\hbar \sum_i^{n} r_{\alpha i} \frac{\partial}{\partial r_{\alpha i}} \quad (\alpha = x, y, z)$$

To evaluate $\left[ \hat{H}, \hat{A} \right]$ we use

$$\left[ \hat{H}, \sum_i^{n} \hat{r}_{\alpha i} \hat{p}_{\alpha i} \right] = \sum_i^{n} \left\{ \left[ \hat{H}, \hat{r}_{\alpha i} \hat{p}_{\alpha i} \right] \pm \hat{r}_{\alpha i} \hat{H} \hat{p}_{\alpha i} \right\}$$

$$= \sum_i^{n} \hat{r}_{\alpha i} \left[ \hat{H}, \hat{p}_{\alpha i} \right] + \sum_i^{n} \left[ \hat{H}, \hat{r}_{\alpha i} \right] \hat{p}_{\alpha i}$$

VHFT
\[
\left[ \hat{H}, \sum_{i} \hat{r}_{\alpha i} \hat{p}_{\alpha i} \right] = i\hbar \sum_{i} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} - i\hbar \sum_{i} \frac{1}{m_i} \hat{p}_{\alpha i}^2
\]

\[
= i\hbar \sum_{i} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} - 2i\hbar \hat{T}
\]

Substitution of the last identity into the integral gives

\[
\int \psi_n^* \left\{ i\hbar \sum_{i} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} - 2i\hbar \hat{T} \right\} \psi_n \, d\tau = 0
\]

\[
\left\langle \psi_n \left| \sum_{i} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} \right| \psi_n \right\rangle = 2 \left\langle \psi_n \left| \hat{T} \right| \psi_n \right\rangle
\]

Using quantum-mechanical averages, we write

\[
\left\langle \sum_{i} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} \right\rangle = 2 \langle T \rangle
\]

which is the quantum-mechanical virial theorem
If \( V \) is a homogeneous function of degree \( g \) when expressed in Cartesian coordinates, Euler’s theorem on homogeneous function gives

\[
\sum_{i}^{n} r_{\alpha i} \frac{\partial V}{\partial r_{\alpha i}} = gV
\]

and the virial theorem simplify to

\[ g \langle V \rangle = 2 \langle T \rangle \]

For a bound stationary state \( E = \langle T \rangle + \langle V \rangle \) we can write virial theorem in two other forms

\[ \langle V \rangle = \frac{2E}{g + 2} \]

\[ \langle T \rangle = \frac{gE}{g + 2} \]
For the H atom, \( V = -\frac{e^2}{(x^2 + y^2 + z^2)^{1/2}} \) is a homogeneous function of degree \( g = -1 \).

For a many-electron atom with spin-orbit interaction neglected, it can be easily shown that \( V \) is still a homogeneous function of degree \( g = -1 \). Hence, for any atom

\[
2 \langle T \rangle = -\langle V \rangle, \quad \text{(spin-orbit interaction neglected)}
\]

For a molecule in the Born-Oppenheimer approximation, \( V \equiv V_{el} \) is a homogeneous function of degree \( g = -1 \) only when \( V_{el} \) is a function of both the electronic and the nuclear Cartesian coordinates.

In such a case, the molecular electronic virial theorem contains an extra term

\[
2 \langle T_{el} \rangle = - \langle V_{el} \rangle - \sum_{I}^{N} R_{\alpha I} \frac{\partial E_{el}}{\partial R_{\alpha I}}
\]
Using

\[ V = V_{el} + V_{NN} \quad , \quad U(R_{\alpha I}) = E_{el}(R_{\alpha I}) + V_{NN} \]

the virial theorem takes the form

\[ 2 \left\langle T_{el} \right\rangle = - \left\langle V \right\rangle - \sum_{I}^{N} R_{\alpha I} \frac{\partial U}{\partial R_{\alpha I}} \]
The Virial Theorem and Chemical Bonding

We now use the virial theorem to examine the changes in electronic kinetic and potential energy that occur when a covalent chemical bond is formed in a diatomic molecule. For formation of a stable bond, the $U(R)$ curve must have a substantial minimum. At this minimum we have

\[
\frac{dU}{dR}\bigg|_{R_e} = 0
\]

\[
2 \langle T_{el} \rangle|_{R_e} = - \langle V \rangle|_{R_e}
\]

\[
\langle T_{el} \rangle|_{R_e} = -U(R_e)
\]

\[
\langle V \rangle|_{R_e} = 2U(R_e)
\]

At $R = \infty$ we have the separated atoms

\[
2 \langle T_{el} \rangle|_{\infty} = - \langle V \rangle|_{\infty}
\]

\[
\langle T_{el} \rangle|_{\infty} = -U(\infty)
\]

\[
\langle V \rangle|_{\infty} = 2U(\infty)
\]
$U(\infty)$ is the sum of the energies of the two separated atoms. For bonding, we have $U(R_e) < U(\infty)$. Therefore,

$$\langle T_{el}\rangle|_{R_e} - \langle T_{el}\rangle|_{\infty} = U(\infty) - U(R_e) > 0$$
$$\langle V\rangle|_{R_e} - \langle V\rangle|_{\infty} = 2 [U(R_e) - U(\infty)] < 0$$

The decrease in potential energy is twice the increase in kinetic energy, and results from allowing the electrons to feel the attractions of both nuclei and perhaps from an increase in orbital exponents in the molecule. The equilibrium dissociation energy is

$$D_e = U(\infty) - U(R_e) = \frac{1}{2} [\langle V\rangle|_{\infty} - \langle V\rangle|_{R_e}]$$
Consider the behaviour of the average potential and kinetic energies for large $R$.

The interactions between atoms at large distances are called *van der Waals* forces. For two neutral atoms, at least one of which is in an $S$ state, quantum-mechanical perturbation theory shows that the van der Waals force of attraction is proportional to $\frac{1}{R^7}$, and the potential energy behaves like

$$U(R) \approx U(\infty) - \frac{A}{R^6}, \quad (R \text{ large})$$

where $A$ is a positive constant. This expression was first derived by London, and van der Waals forces between neutral atoms are called London forces or dispersion forces.
Energy vs. $R$ graph with

- $\langle T_{el} \rangle$,
- $U(R)$,
- $\langle V \rangle$,
- $\langle T_{el} \rangle|_\infty = 1$,
- $U(\infty) = -1$,
- $\langle V \rangle|_\infty = -2$.
THE HELLMANN-FEYNMAN THEOREM

Consider a system with a time-independent Hamiltonian $\hat{H}$ that involves parameters. An obvious example is the molecular electronic Hamiltonian that depends parametrically on the nuclear coordinates.

We begin with the Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$ where the $\psi_n$'s are the normalized stationary-state eigenfunctions. Because of normalization, we have

$$E_n = \left\langle \psi_n \right| \hat{H} \left| \psi_n \right\rangle$$

$$\frac{\partial E_n}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left\langle \psi_n \right| \hat{H} \left| \psi_n \right\rangle$$
Provided the integrand is well behaved

\[
\frac{\partial E_n}{\partial \lambda} = \int \frac{\partial}{\partial \lambda} (\psi_n^* \hat{H} \psi_n) d\tau = \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau + \int \psi_n^* \frac{\partial}{\partial \lambda} (\hat{H} \psi_n) d\tau
\]

The potential-energy operator is just multiplication by \( V \), so

\[
\frac{\partial}{\partial \lambda} (\hat{V} \psi_n) = \frac{\partial V}{\partial \lambda} \psi_n + V \frac{\partial \psi_n}{\partial \lambda}
\]

The parameter \( \lambda \) will occur in the kinetic-energy operator as part of the factor multiplying one or more of the derivatives with respect to the coordinates. Since we can change the order of the partial differentiations without affecting the result, we can write

\[
\frac{\partial}{\partial \lambda} (\hat{T} \psi_n) = \frac{\partial \hat{T}}{\partial \lambda} \psi_n + \hat{T} \frac{\partial \psi_n}{\partial \lambda}
\]

where \( \frac{\partial \hat{T}}{\partial \lambda} \) is found by differentiating \( \hat{T} \) with respect to \( \lambda \) just as if it were a function instead of an operator.
Combining the two pieces, we can write

\[ \frac{\partial}{\partial \lambda} (\hat{H} \psi_n) = \frac{\partial \hat{H}}{\partial \lambda} \psi_n + \hat{H} \frac{\partial \psi_n}{\partial \lambda} \]

Therefore

\[ \frac{\partial E_n}{\partial \lambda} = \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau + \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau + \int \psi_n^* \hat{H} \frac{\partial \psi_n}{\partial \lambda} d\tau \]

For the first integral we have

\[ \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau = E_n \int \frac{\partial \psi_n^*}{\partial \lambda} \psi_n d\tau \]

For the last integral we have

\[ \int \psi_n^* \hat{H} \frac{\partial \psi_n}{\partial \lambda} d\tau = \int \frac{\partial \psi_n}{\partial \lambda} (\hat{H} \psi_n)^* d\tau = E_n \int \psi_n^* \frac{\partial \psi_n}{\partial \lambda} \]

VHFT
Substitution gives

\[
\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau + E_n \left( \int \frac{\partial \psi_n^*}{\partial \lambda} \psi_n d\tau + \int \psi_n^* \frac{\partial \psi_n}{\partial \lambda} \right)
\]

\[
\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau + E_n \left( \frac{\partial}{\partial \lambda} \int \psi_n^* \psi_n d\tau \right)
\]

The wave function is normalized; hence

\[
\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau
\]

The last equation is the **generalized Hellmann-Feynman theorem**.

The first-order perturbation theory result is a special case of the Hellmann-Feynman theorem. The Hellmann-Feynman theorem with $E_n$ being the Hartree-Fock energy is obeyed by Hartree-Fock (as well as exact) wave functions.
THE ELECTROSTATIC THEOREM

Hellmann and Feynman independently applied the theorem to molecules taking $\lambda$ as a nuclear Cartesian coordinate.

In the Born-Oppenheimer approximation, the electronic Schrödinger equation for a fixed nuclear configuration is

$$\hat{H}\psi_{el} = (\hat{T}_{el} + \hat{V})\psi_{el} = U\psi_{el}$$

where

$$\hat{V} = \hat{V}_{el} + \hat{V}_{NN}$$
The Hamiltonian \( \hat{H} \) depends on the nuclear coordinates as parameters. If \( x_\delta \) is the \( x \) coordinate of nucleus \( \delta \), the generalized Hellmann-Feynman theorem gives

\[
\frac{\partial U}{\partial x_\delta} = \int \psi^*_\text{el} \frac{\partial \hat{H}}{\partial x_\delta} \psi_{\text{el}} d\tau_{\text{el}}
\]

The kinetic-energy part of \( \hat{H} \) is independent of the nuclear Cartesian coordinates. Hence

\[
\frac{\partial U}{\partial x_\delta} = \int \psi^*_\text{el} \frac{\partial V}{\partial x_\delta} \psi_{\text{el}} d\tau_{\text{el}}
\]

We have

\[
\frac{\partial V}{\partial x_\delta} = \frac{\partial V_{\text{el}}}{\partial x_\delta} + \frac{\partial V_{\text{NN}}}{\partial x_\delta}
\]
In atomic units

\[ V_{\text{el}} = - \sum_{\alpha} \sum_{i} \sum_{n} \frac{Z_{\alpha}}{r_{i\alpha}} \]

\[ V_{\text{el}} = - \sum_{\alpha} \sum_{i} \sum_{n} \frac{Z_{\alpha}}{[\left(x_{i} - x_{\alpha}\right)^{2} + \left(y_{i} - y_{\alpha}\right)^{2} + \left(z_{i} - z_{\alpha}\right)^{2}]^{1/2}} \]

\[ \frac{\partial V_{\text{el}}}{\partial x_{\delta}} = - \sum_{i} \frac{Z_{\delta} \left(x_{i} - x_{\delta}\right)}{[\left(x_{i} - x_{\delta}\right)^{2} + \left(y_{i} - y_{\delta}\right)^{2} + \left(z_{i} - z_{\delta}\right)^{2}]^{3/2}} \]

\[ \frac{\partial V_{\text{el}}}{\partial x_{\delta}} = - \sum_{i} \frac{Z_{\delta} \left(x_{i} - x_{\delta}\right)}{r_{i\delta}^{3}} \]
\[ V_{NN} = \sum_{\alpha} \sum_{\beta > \alpha}^{N} \frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}} \]

\[ V_{NN} = \sum_{\alpha} \sum_{\beta > \alpha}^{N} \frac{Z_{\alpha}Z_{\beta}}{\left[ \left( x_{\alpha} - x_{\beta} \right)^2 + \left( y_{\alpha} - y_{\beta} \right)^2 + \left( z_{\alpha} - z_{\beta} \right)^2 \right]^{1/2}} \]

\[ \frac{\partial V_{NN}}{\partial x_{\delta}} = \frac{\partial}{\partial x_{\delta}} \sum_{\alpha \neq \delta}^{N} \frac{Z_{\alpha}Z_{\delta}}{\left[ \left( x_{\alpha} - x_{\delta} \right)^2 + \left( y_{\alpha} - y_{\delta} \right)^2 + \left( z_{\alpha} - z_{\delta} \right)^2 \right]^{1/2}} \]

\[ \frac{\partial V_{NN}}{\partial x_{\delta}} = \sum_{\alpha \neq \delta}^{N} \frac{Z_{\alpha}Z_{\delta}(x_{\alpha} - x_{\delta})}{\left[ \left( x_{\alpha} - x_{\delta} \right)^2 + \left( y_{\alpha} - y_{\delta} \right)^2 + \left( z_{\alpha} - z_{\delta} \right)^2 \right]^{3/2}} \]

\[ \frac{\partial V_{NN}}{\partial x_{\delta}} = \sum_{\alpha \neq \delta}^{N} \frac{Z_{\alpha}Z_{\delta}(x_{\alpha} - x_{\delta})}{r^{3}_{\alpha\delta}} \]
Since $\partial V_{NN}/\partial x_\delta$ does not involve the electronic coordinates and $\psi_{el}$ is normalized, after substitution in the integral we have

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta \int |\psi_{el}|^2 \sum_{i}^n \frac{x_i - x_\delta}{r_{i\delta}^3} d\tau_{el} + Z_\delta \sum_{\alpha \neq \delta}^N Z_\alpha \frac{x_\alpha - x_\delta}{r_{\alpha\delta}^3}$$

which can be written using the electron probability density function as

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta \int \rho(r) \frac{x - x_\delta}{|r - r_\delta|^3} dr + Z_\delta \sum_{\alpha \neq \delta}^N Z_\alpha \frac{x_\alpha - x_\delta}{|r_\alpha - r_\delta|^3}$$

The quantity $-\partial U/\partial x_\delta$ can thus be viewed as the $x$ component of the effective force on nucleus $\delta$ due to the other nuclei and the electrons.

Actually, we have two corresponding equations for $\partial U/\partial y_\delta$ and $\partial U/\partial z_\delta$. 
If $F_\delta$ is the effective force on nucleus $\delta$, then

$$F_\delta = -\nabla_\delta U = -i \frac{\partial U}{\partial x_\delta} - j \frac{\partial U}{\partial y_\delta} - k \frac{\partial U}{\partial z_\delta}$$

$$F_\delta = -Z_\delta \int \rho(r) \frac{r_\delta - r}{|r - r_\delta|^3} \, dr + Z_\delta \sum_{\alpha \neq \delta} Z_\alpha \frac{r_\delta - r_\alpha}{|r_\alpha - r_\delta|^3}$$

Thus the effective force acting on a nucleus in a molecule can be calculated by simple electrostatics as the sum of the Coulombic forces exerted by the other nuclei and by a hypothetical electron cloud whose charge density $-\rho(r)$ is found by solving the electronic Schrödinger equation.

This is the **Hellmann-Feynman electrostatic theorem**.
At the equilibrium geometry the effective force on each nucleus is zero, as the derivatives of $U$ respect to all nuclear Cartesian coordinates are vanishing. Then, the hypothetical electron smear must exert on each nucleus a net attractive Hellmann-Feynman force to counterbalance the internuclear repulsion.

From the Hellmann-Feynman viewpoint, we seem to be considering chemical bonding solely in terms of potential energy, whereas the virial-theorem discussion involved both potential and kinetic energy. The use of the electrostatic theorem to explain chemical bonding has been criticized by some quantum chemists on the grounds that it hides the role of kinetic energy in bonding.
Books

- Schiff L. I. “Quantum Mechanics” McGraw-Hill
- Levine I. N. “Quantum Chemistry” Prentice-Hall