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# Physical Review A

## GENERAL PHYSICS

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#### Hellmann-Feynman Theorem in Thomas-Fermi and Related Theories

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The general Heilmann-Feynman theorem (derivative of energy with respect to a parameter = expectation value of derivative of Hamiltonian) is proved for theories in which the electron density is determined by making the energy functional stationary. Some simple applications are given.

Recently, Teller<sup>1</sup> and Balàzs<sup>2</sup> have given arguments showing that the various quantum-statistical theories<sup>3</sup> [Thomas-Fermi (TF), Thomas-Fermi-Dirac (TFD), Thomas-Fermi-Dirac-Gombas] cannot give a stable molecule. [Sheldon's TFD calculations<sup>4</sup> on  $N_2$  (the only true molecular calculations using the exact theory) had previously led to instability.] Teller<sup>1</sup> showed that the energy of a molecular system in these theories will never be lower than the energy of the separated atoms; Balàzs<sup>2</sup> showed that the forces on the nuclei always tend to dissociate the molecule. The equivalence of these two points of view is part of the content of the Hellmann-Feynman theorem.<sup>5,6</sup>

The theorem in its general form states that the change in the energy with a parameter appearing in the Hamiltonian can be obtained from the expectation value of the derivative of the Hamiltonian with respect to this parameter. For the usual quantum-mechanical situation, the exact energy is the eigenvalue of a many-electron Hamiltonian, and expectation values are over a many-electron wave function; in the quantum-statistical theories, the electron density is obtained from a nonlinear equation, and there is no wave function. However, we note that a proof of the theorem can be based on the variational principle.<sup>6</sup> This suggests, for the statistical theories, a related proof of the theorem.

We give a proof here for the general Hellmann-Feynman theorem which applies to a class of theories including the quantum-statistical ones. We then mention some of the implications. We assume that the energy is given as a functional E of the electron density  $\rho$ . E may also depend on a parameter P. The density is determined by making the functional stationary to variations of  $\rho$ , with any auxiliary condition on  $\rho$  being taken into account by a Lagrange multiplier  $\lambda$ :

$$\delta[E(\rho, P) + \lambda A(\rho)] = 0.$$
(1)

The density thus determined for a given P is denoted by  $\rho_P$  and the corresponding energy by  $E_P = E(\rho_P, P)$ . The energy derivative  $dE_P/dP$  has two parts, due to the explicit occurrence of P in E and due to the dependence of  $\rho_P$  on P. If, as is usually the case, P appears in an expectation value as  $\int F(P)f(\rho) d\tau$ , the first part of  $dE_P/dP$  will be the expectation value of the derivative,  $\int F'(P)f(\rho)d\tau$ . The second part of  $dE_P/dP$  can be written  $\lim(\delta P \to 0)[E(\rho_{P+\delta P}, P) - E(\rho_P, P)]/\delta P$ . But  $E(\rho_P, P)$  is stationary to any variation in  $\rho$  which leaves  $A(\rho)$  invariant, so this second term vanishes. This proves our theorem. We now give several illustrations of it.

If P is a nuclear charge, it appears as  $Pe^2 \int r^{-1} \times \rho(\mathbf{\dot{r}}) d\tau$ , where r is the distance from the nucleus. Then dE/dP is given by  $e^2 \int r^{-1} \rho(\mathbf{\dot{r}}) d\tau$ , as may be shown by direct (but more complicated) manipulation<sup>7</sup> of the energy functional. If P is a nuclear coordinate, the theorem states that dE/dP is given by  $\int (\partial V_{nuc} / \partial P) \rho d\tau$ , where the derivative of the electron-nuclear potential energy operator is taken with electronic coordinates held fixed. The equivalence of energy derivative and expectation value of electrostatic force, referred to above,

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follows when the electrons are fixed in a spacefixed coordinate system. For a diatomic, one may use confocal ellipsodial coordinates, in which interparticle distances are proportional to the internuclear distance R for fixed values of these coordinates. The volume element is *explicitly* proportional to  $R^3$ ,  $\rho$  to  $R^{-3}$ , the potential-energy operators to  $R^{-1}$ . Taking P = R, we note that the potential-energy terms V are explicitly proportional to  $R^{-1}$  and the kinetic energy T (proportional to  $\int \rho^{5/3} d\tau$ ) to  $R^{-2}$ . Then our theorem gives

$$dE/dR = -R^{-1}V - 2R^{-1}T , \qquad (2)$$

which is the virial theorem. This proof is well known for the quantum mechanical case.<sup>8</sup> The atom is the special case where one nuclear charge is zero; E then does not depend on R.

As a final example, the change in energy in going from the TF to the TFD theory is due to the additional term  $-\kappa_a \int \rho^{4/3} d\tau$  in the energy functional, with  $\kappa_a \sim 0.74 e^2$ . The energy change could be estimated from the TF function without computing the TFD function by considering *E* as a function of  $\kappa_a$ , with  $\kappa_a = 0$  corresponding to TF and  $\kappa_a \sim 0.74e^2$ to TFD. Imagine  $E(\kappa_a)$  to be expanded in a power series about  $\kappa_a = 0$ . If the linear term suffices, the energy change is  $\kappa_a dE/d\kappa_a = -\kappa_a \int \rho^{4/3} d\tau$ , where  $\rho$  is the TF density. We obtain then

$$E_{\rm TFD} - E_{\rm TF} = -0.363 Z^{5/3} \int \varphi^2 dx \, e^2 / a_0 \,, \qquad (3)$$

where  $\varphi$  is the solution to the TF equation.<sup>3</sup> Evaluating the integral numerically for the tabulated  $\varphi$  gives 0.640, and the energy difference is  $-0.232 \times Z^{5/3} e^2/a_0$ , as compared to  $-0.23Z^{5/3} e^2/a_0$ , as calculated directly by Gombas<sup>9</sup> [If the expansion of  $E(\kappa_a)$  were made around  $\kappa_a = 0.74e^2$  instead of 0, the same reasoning would show the energy difference could be calculated from  $\kappa_a \int \rho^{4/3} d\tau$  where  $\rho$  is the TFD density.]

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<sup>3</sup>P. Gombás, Die Statistische Theorie des Atoms und

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<sup>5</sup>R. P. Feynman, Phys. Rev. <u>56</u>, 340 (1939).
<sup>6</sup>H. Hellmann, *Einführung in die Quantenchemie*

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(Deuticke, Leipzig, 1937).

<sup>7</sup>Reference 3, p. 59.

<sup>8</sup>For example, A. C. Hurley in *Molecular Orbitals in Chemistry, Physics and Biology* (Academic, New York, 1964), p. 161.

<sup>9</sup>Reference 3, p. 90.

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### Padé Approximants and Inner Projections in the Brillouin-Wigner Perturbation Scheme for He-like Ions\*

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The continued-fraction expansions in terms of Brillouin-Wigner perturbation energies are evaluated for the He-like series. They show remarkable convergence and stability properties. Both Padé approximants and perturbation energies are computed with formulas derived by the inner-projection technique.

#### INTRODUCTION

The Brillouin-Wigner (BW) perturbation series<sup>1</sup> suffers from convergence problems which, in addition to computational difficulties, made its use relatively infrequent. Modifications of the scheme, which cast it into a continued fraction expansion were made by Feenberg and others.<sup>2-4</sup> It is possible to derive the bounding properties of the alternate energy approximants of Young *et al.*<sup>3</sup>

by showing that they can be obtained by inner projections of the reaction operator in the way suggested by Löwdin, <sup>5</sup> provided one chooses the linear manifold considered in a specific way.<sup>6</sup> It can be seen that the upper- and lower-bound approximants can be identified as Padé approximants<sup>7</sup> to the BW series.<sup>8</sup> In the Rayleigh-Schrödinger (RS) case, the analogous Padé approximants showed remarkable convergence even though one could