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Jerry Goodisman  
*Syracuse University*

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# PHYSICAL REVIEW A

## GENERAL PHYSICS

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

Jerry Goodisman

*Department of Chemistry, Syracuse University, Syracuse, New York 13210*

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The general Hellmann-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 Balázs<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; Balázs<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 as-

sume 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  $\lambda$ :

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

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  $\lim(\delta P \rightarrow 0)[E(\rho_{P+\delta P}, P) - E(\rho_P, P)]/\delta P$ . 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  $Pe^2 \int r^{-1} \times \rho(\vec{r})d\tau$ , where  $r$  is the distance from the nucleus. Then  $dE/dP$  is given by  $e^2 \int r^{-1} \rho(\vec{r})d\tau$ , 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  $\int (\partial V_{\text{nuc}}/\partial P)\rho d\tau$ , where the derivative is 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,

follows when the electrons are fixed in a space-fixed coordinate system. For a diatomic, one may use confocal ellipsoidal 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

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

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  $\kappa_a \sim 0.74 e^2$  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

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

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  $-0.23 Z^{5/3} e^2/a_0$ , as calculated directly by Gombas<sup>9</sup> [If the expansion of  $E(\kappa_a)$  were made around  $\kappa_a = 0.74 e^2$  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.]

<sup>1</sup>E. Teller, *Rev. Mod. Phys.* **34**, 627 (1962).

<sup>2</sup>N. L. Balázs, *Phys. Rev.* **156**, 42 (1967).

<sup>3</sup>P. Gombás, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer, Vienna, 1949).

<sup>4</sup>J. W. Sheldon, *Phys. Rev.* **99**, 1291 (1955).

<sup>5</sup>R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

<sup>6</sup>H. Hellmann, *Einführung in die Quantenchemie*

(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.

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

G. L. Bendazzoli,† O. Goscinski, and G. Orlandi‡

*Department of Quantum Chemistry, University of Uppsala, Uppsala, Sweden*

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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