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An Introduction To Hellmann-feynman Theory

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by

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ABSTRACT

The Hellmann-Feynman theorem is presented together with certain allied theorems. The origin of the Hellmann-Feynman theorem in quantum physical chemistry is described. The theorem is stated with proof and with discussion of applicability and reliability. Some adaptations of the theorem to the study of the variation of zeros of special functions and orthogonal polynomials are surveyed. Possible extensions are discussed.

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Chapter 1

Introduction

Briefly stated, the Hellmann-Feynman theorem assures that a non-degenerate eigenvalue of a hermitian operator in a parameter dependent eigensystem varies with respect to the parameter according to the formula

$$\frac{\partial E_\nu}{\partial \nu} = \left\langle \psi_\nu, \frac{\partial \mathsf{H}_\nu}{\partial \nu} \psi_\nu \right\rangle, \tag{1.1}$$

provided that the associated normalized eigenfunction, ψ_ν, is continuous with respect to the parameter, ν.

Neither Feynman nor Hellmann was first to prove it. Beyond that, the origin of the Hellmann-Feynman theorem is a somewhat clouded history. The formula (1.1) and allied formulas seem to have first appeared around 1930 with the advent of quantum mechanics. Researchers involved in the new and exciting field were innovative[1]. Some innovations came into widespread use without attribution of origin. A protegé of Wolfgang Pauli named Paul Güttinger may have been the first to publish [13] a careful derivation of the Hellmann-Feynman formulas, but precursors had appeared at least as early as 1922, see figure 1.

Richard P. Feynman is widely-known, but Hellmann is relatively unknown. Hans G. A.

[1]When Heisenberg published his 1926 paper on quantum mechanics, he did so without prior knowledge of the mathematics of matrices. It was only later recognized that the operations Heisenberg described were the same as matrix multiplication.

(a) Pauli (1922) [30]:

$$\delta E = \frac{\partial H(p,q,\nu)}{\partial \nu}\delta\nu$$

(b) Schrödinger (1926) [33]:

$$\delta E_k = \langle \psi_k, \delta \mathsf{H} \psi_k \rangle$$

(c) Born and Fock (1928) [2]:

$$\left\langle \psi_m(s), \frac{d\psi_n(s)}{ds} \right\rangle (E_n(s) - E_m(s)) = \left\langle \psi_m(s), \frac{d\mathsf{H}(s)}{ds}\psi_n(s) \right\rangle$$

(d) Güttinger (1931) [13]:

$$\text{If} \quad m \neq n, \quad \frac{h}{2\pi i}\left[\left(\frac{\partial H}{\partial \nu}\right)_{p,q}\right]_{m,n} = k_{m,n}(E_n - E_m)$$

$$\text{and if} \quad m = n, \quad \text{then,} \quad \left[\left(\frac{\partial H}{\partial \nu}\right)_{p,q}\right]_{m,m} = \frac{\partial E_m}{\partial \nu}$$

Figure 1.1: Published antecedents of the Hellmann-Feynman formulas appeared as early as 1922, [Notation has been altered.] [31]

Hellmann was a physicist well versed in chemistry. After taking a doctorate in physics from the University of Stuttgart[2], in 1929, he accepted a lectureship in Hannover[3]and devoted himself to the mastery of quantum chemistry. He first published his statement and proof of the Hellmann-Feynman theorem in 1933 [15], and included the same in his manuscript of a quantum chemistry textbook. Unfortunately, Hellmann was an outspoken antifascist whose protestant wife was of jewish descent; by early 1934 he could no longer publish in Germany. His lectureship was terminated. He emigrated to Moscow, where his wife had relatives, and there secured a position as head of the theory group at the Karpov Institute of

[2]Institut für Theoretische und Angewandte Physik der Universität Stuttgart—the Institute for Theoretical and Applied Physics of the University of Stuttgart. Hellmann's dissertation, under advisor Erich Regener, was on photochemistry of stratospheric ozone.

[3]At first, Hellmann was an assistant to professor of theoretical physics Erwin Fues at the Technische Hochschule. Later, 1931, he secured the lectureship in physics at the veterinary college (Tierärztliche Hochschule) in Hannover.

Physical Chemistry[4]. Three colleagues at the institute translated his book, and it appeared in Russian, in 1937 [19], with added explanatory material to make it more accessible. It quickly sold out. A more compact and demanding German version [18], finally found a publisher in Austria that same year[5]. At the Karpov Institute Hellmann mentored Nicolai D. Sokolov, later acknowledged as the foremost quantum chemist in the Soviet Union [35]. Hellmann was productive for three years in Moscow and, by communications [16] [17] posted in English language journals, attempted to call attention to his work, mostly written in German. With war threatening, persons of foreign nationality came under suspicion in Russia; Hellmann's nationality doomed him. Early in 1938, an ambitious colleague at the institute denounced Hellmann to promote his own career. Hellmann was arrested in the night of March 9, 1938. To mention or cite Hellmann became unsafe; he was nearly forgotten in Russia. Even his family knew nothing of his subsequent fate until 1989; Hellmann had been forced to a false confession of espionage and had been executed, a victim of the Stalinist purges. Hellmann was 35 years of age [31] [10] [11].

Feynman was an undergraduate at MIT, in 1939, when John C. Slater suggested that he try to prove the Hellmann-Feynman theorem, by then in widespread use. The proof became Feynman's undergraduate thesis and a well-known journal article, "Forces in Molecules" [12]. No references are cited, but Feynman expressed gratitude to Slater and to W. Conyers Herring, then a postdoctoral fellow under Slater. The "Forces in Molecules" paper also mentions van der Waals forces, a area of special interest to Herring and Slater. None of the three were aware of Hellmann's proof [34]. Hellmann, on the other hand, cited work of Slater in the very paper in which his proof appeared, and also in 1937 with comment on a work of Fritz London about molecular and van der Waals forces [17].

Slater's notion that the Hellmann-Feynman theorem was a surmise in need of a proof was not a common sentiment. Rather it was widely regarded as a routine application of

[4]Before emigrating, Hellmann had several offers of positions outside Germany, three in the Soviet Union and one in the United States [10].

[5]With wartime disregard for copyright, the German version was replicated in America, in 1944 [20].

perturbation technique to the problem of solving the Schrödinger equation for a molecule,

$$\mathsf{H}\psi = E\psi, \tag{1.2}$$

an n-body problem not in general solvable analytically. The eigenfunction, ψ, is always normalized because ψ^2 is a distribution in phase space of the n-bodies; it is a real-valued function of vectors. The operator is a symmetric Hamiltonian operator. The eigenvalue E is the energy. The Born-Oppenheimer approximation [3] to the problem restricts the domain of ψ by assigning fixed positions to the nuclei so ψ represents distribution of electrons only; thus, positions of nuclei become parameters of the system. The eigenfunction solution, ψ_ν, of the Born-Oppenheimer approximation for a given nuclear configuration is data input to the Hellmann-Feynman formula.

$$\frac{\partial E_\nu}{\partial \nu} = \left\langle \psi_\nu, \frac{\partial \mathsf{H}_\nu}{\partial \nu}\psi_\nu \right\rangle,$$

By considering E_ν as the potential energy of the nuclear configuration, the generalized force toward another configuration is given by the derivative, $-\frac{\partial E_\nu}{\partial \nu}$, or for vector ν the gradient $-\nabla_\nu E_\nu$, toward an equilibrium configuration in the Born-Oppenheimer approximation where forces would vanish.

The Hellmann-Feynman theorem is much used in quantum chemistry. Feynman's "Forces in Molecules" has been cited over 1200 times. Often claims of its failures appear, generally either because of insufficiently good approximation of ψ or because of failure to fulfill sufficient conditions for its application. Beginning in 1975, mathematicians began using the Hellmann-Feynman theorem as a tool in the study variation with respect to a parameter of zeros of orthogonal polynomials and special functions.

Throughout this work I shall prefer inner product notation, as above, to integral notation, $\frac{\partial E_\nu}{\partial \nu} = \int_\tau \psi_\nu \frac{\partial \mathsf{H}_\nu}{\partial \nu}\overline{\psi_\nu} d\tau$, and to Bra-Ket notation of Dirac, $\frac{\partial E_\nu}{\partial \nu} = \langle \psi_\nu | \frac{\partial \mathsf{H}_\nu}{\partial \nu} | \psi_\nu \rangle$, both commonly used in the literature of quantum physics and chemistry. See the appendix about notation.

Chapter 2

Statement and Proof

The Hellmann-Feynman theorem with one-dimensional variation is here stated with proof, from Mourad E. H. Ismail and Ruiming Zhang [26].

THEOREM: Let S be an inner product space with inner product $\langle \cdot, \cdot \rangle_\nu$, possibly depending on a parameter, $\nu \in I = (a, b)$. Let H_ν be a symmetric operator on S and assume that ψ_ν is an eigenfunction of H_ν corresponding to an eigenvalue λ_ν. Further assume that

$$\lim_{\mu \to \nu} \langle \psi_\mu, \psi_\nu \rangle_\nu = \langle \psi_\nu, \psi_\nu \rangle_\nu > 0 \tag{2.1}$$

and that

$$\lim_{\mu \to \nu} \left\langle \left(\frac{\mathsf{H}_\mu - \mathsf{H}_\nu}{\mu - \nu} \right) \psi_\mu, \psi_\nu \right\rangle_\nu \text{ exists.} \tag{2.2}$$

If we define $\frac{\partial \mathsf{H}_\nu}{\partial \nu}$ by

$$\left\langle \frac{\partial \mathsf{H}_\nu}{\partial \nu} \psi_\nu, \psi_\nu \right\rangle_\nu := \lim_{\mu \to \nu} \left\langle \left(\frac{\mathsf{H}_\mu - \mathsf{H}_\nu}{\mu - \nu} \right) \psi_\mu, \psi_\nu \right\rangle_\nu \tag{2.3}$$

then $d\lambda_\nu / d\nu$ exists for $\nu \in (a, b)$ and is given by

$$\frac{d\lambda_\nu}{d\nu} = \frac{\left\langle \frac{\partial \mathsf{H}_\nu}{\partial \nu} \psi_\nu, \psi_\nu \right\rangle_\nu}{\langle \psi_\nu, \psi_\nu \rangle_\nu} \tag{2.4}$$

PROOF: Clearly, $\mathsf{H}_\mu\psi_\mu = \lambda_\mu\psi_\mu$ implies

$$\langle \mathsf{H}_\mu\psi_\mu, \psi_\nu\rangle_\nu = \lambda_\mu\langle\psi_\mu, \psi_\nu\rangle_\nu.$$

Hence

$$(\lambda_\mu - \lambda_\nu)\langle\psi_\mu, \psi_\nu\rangle_\nu = \langle \mathsf{H}_\mu\psi_\mu, \psi_\nu\rangle_\nu - \langle\psi_\mu, \mathsf{H}_\nu\psi_\nu\rangle_\nu. \tag{2.5}$$

The symmetry of the operator H_ν implies

$$(\lambda_\mu - \lambda_\nu)\langle\psi_\mu, \psi_\nu\rangle_\nu = \langle(\mathsf{H}_\mu - \mathsf{H}_\nu)\psi_\mu, \psi_\nu\rangle_\nu. \tag{2.6}$$

We now divide by $\mu - \nu$ and then let $\mu \to \nu$ in (2.6). The limit of the right-hand side of (2.6) exists, for $\nu \in I$, and equals

$$\left\langle \frac{\partial \mathsf{H}_\nu}{\partial \nu}\psi_\nu, \psi_\nu \right\rangle_\nu \tag{2.7}$$

while the second factor on the left side tends to the positive number $\langle\psi_\nu, \psi_\nu\rangle_\nu$ as $\mu \to \nu$, $\nu \in I$. Thus the limit of the remaining factor exists and (2.4) holds. This completes the proof. □

The significance of the definition of the derivative of the operator, equation (2.3), warrants emphasis. It is innovative and not equivalent to earlier usage, which was that of a Fréchet differential, defined by $\frac{\partial \mathsf{H}_\nu}{\partial \nu} = A$ such that

$$\lim_{h\to 0} \sup_{\psi\in S} \frac{||\frac{\mathsf{H}_{\nu+h} - \mathsf{H}_\nu}{h}\psi - A\psi||}{||\psi||} = 0$$

with concomitant questions of existence that the new definition avoids. Clearly, conformity to the new definition in writing the derivative of the operator is required.

The theorem can readily be generalized for n-dimensional ν.

$$\nabla_\nu \lambda_\nu = \nabla_\nu \left\langle \mathsf{H}_\nu \psi_\nu, \psi_\nu \right\rangle_\nu = \sum_{k=1}^{n} \left\langle \frac{\partial \mathsf{H}_\nu}{\partial \nu_k} \psi_\nu, \psi_\nu \right\rangle_\nu \hat{\nu}_k \tag{2.8}$$

where $\hat{\nu}_k$ denotes the k^{th} unit basis vector of ν. Recalling the origin of ν, realize that to restore ν further amounts to dispensing with the Born-Oppenheimer approximation.

Chapter 3

The Quantum Chemistry Context

3.1 Electrostatic Theorem

"The electrostatic theorem" is an often-used alias for the Hellmann-Feynman theorem. Although quantum chemists frequently employ the Hellmann-Feynman theorem, they often have misconceptions about it. Many believe that it proves that the forces on the nuclei are purely electrostatic forces. Rather, that is the premise for its application, not the conclusion. While the notion that the theorem is obviously true is widely held, challenges to the validity or reliability of the theorem also appear frequently. This is in part attributable to misunderstanding of the theorem. But instability is a serious issue, as Slater has indicated, "...the Hellmann-Feynman theorem has been less [useful]. The reason is that most molecular work has been done with very inaccurate approximations to molecular orbitals." Which is to say, the approximations of ψ are often insufficiently accurate models of the physical system.

As an example of misunderstanding, the objection that the dependence of the operator on a parameter does not guarantee that the eigenvalues and eigenfunctions will be smoothly dependent on the parameter [31] overlooks the corresponding stated requirement, the eigenfunction must be continuous with respect to the parameter.

A second objection, that the derivative of the eigenfunction with respect to the pa-

rameter, $\frac{\partial\psi_\nu}{\partial\nu}$, may lie outside the domain of the operator [31], has its basis in a weakness of earlier proofs, including Feynman's, Hellmann's and Güttinger's, that they did express such a derivative and tacitly assumed its existence and the existence of the integral $\int_\tau \frac{\partial\psi_\nu}{\partial\nu}\mathsf{H}_\nu\overline{\psi}_\nu d\tau = E_\nu \int_\tau \frac{\partial\psi_\nu}{\partial\nu}\overline{\psi}_\nu d\tau$. The arguments ran thus

$$\begin{aligned}
\frac{\partial E_\nu}{\partial\nu} &= \frac{\partial}{\partial\nu}\left\langle \mathsf{H}_\nu\psi_\nu, \psi_\nu\right\rangle \\
&= \left\langle \frac{\partial\mathsf{H}_\nu}{\partial\nu}\psi_\nu, \psi_\nu\right\rangle + \left\langle \frac{\partial\psi_\nu}{\partial\nu}, \mathsf{H}_\nu\psi_\nu\right\rangle + \left\langle \mathsf{H}_\nu\psi_\nu, \frac{\partial\psi_\nu}{\partial\nu}\right\rangle \\
&= \left\langle \frac{\partial\mathsf{H}_\nu}{\partial\nu}\psi_\nu, \psi_\nu\right\rangle + E_\nu\left(\left\langle \frac{\partial\psi_\nu}{\partial\nu}, \psi_\nu\right\rangle + \left\langle \psi_\nu, \frac{\partial\psi_\nu}{\partial\nu}\right\rangle\right)
\end{aligned}$$

where the two rightmost terms are, by various rationales, together equated to zero. Most commonly, as $E_\nu\frac{\partial}{\partial\nu}\left\langle\psi_\nu,\psi_\nu\right\rangle = E_\nu\frac{\partial}{\partial\nu}(1)$, but Hellmann argued that the rightmost two terms were separately zero for extremal E_ν.

The importance of the continuity of ψ_ν with respect to ν must not be overlooked. In particular, degeneracy of eigenvalues gives rise to linear combinations of eigenfunctions that are not continuously dependent on ν. In a condition of degeneracy the eigenfunctions for which the Hellmann-Feynmann theorem holds are not well-defined. A method of handling degeneracy has been described by S. Raj Vatsya [36] in terms of matrices. For an N-fold degeneracy at $\nu = \nu_0$, consider an arbitrary basis vector $\phi_n(\nu_0),\ n = 1, 2, \ldots, N$ of the degenerate eigenspace. Let $\mathsf{P}_N(\nu_0)$ be the orthogonal projection matrix that projects an arbitrary vector of the space onto the degenerate eigenspace. For for a perturbed $\nu \neq \nu_0$, we can write

$$\mathsf{H}(\nu)\mathsf{P}_N(\nu) = E(\nu)\mathsf{P}_N(\nu)$$

with N distinct solutions for $E_n(\nu)$ and corresponding eigenvectors $\phi_n(\nu)$. Differentiating this, left multiplying by $\mathsf{P}_N(\nu)$ and evaluating the result at ν_0 yields a matrix $\mathsf{O}_N(\nu_0)$,

$$\mathsf{O}_N(\nu_0) = \mathsf{P}_N(\nu_0)\frac{\partial\mathsf{H}}{\partial\nu}(\nu_0)\mathsf{P}_N(\nu_0) = \frac{\partial E}{\partial\nu}(\nu_0)\mathsf{P}_N(\nu_0),$$

which has as eigenvalues the correct $\frac{\partial E_n}{\partial \nu}(\nu_0)$ and corresponding eigenvectors of $\mathsf{H}(\nu_0)$.

The theorem does not guarantee stability. This is an important consideration in quantum chemistry applications. The Born-Oppenheimer model is approximate; it is understood that an actual molecule has oscillating nuclei. As data input, ν gives rise to error in ψ_ν, E_ν, and $\frac{\partial E_\nu}{\partial \nu}$. Stability improves as variation of ψ_ν with respect to ν decreases. Andrew C. Hurley has examined the question of stability of the eigenvalue approximations [22] [21]. Relying on differentiability of the wave function, he establishes a criterion for assessing stability and a procedure for minimizing instability. For the ground state of a stable molecular configuration, the Born-Oppenheimer solution coincides with a local stability maximum by Hurley's criterion. Saul T. Epstein has confirmed the applicability of Hurley's criterion for stabilities of several Hellmann-Feynman variants including the integral version (below) and a time-dependent version due to Edward F. Hayes and Robert G. Parr [7] [14].

3.2 Integral Hellmann-Feynman Theorem

An intermediate result in the proof of the Hellmann-Feynman theorem, equation (2.6) reproduced here,

$$(\lambda_\mu - \lambda_\nu)\langle \psi_\mu, \psi_\nu \rangle_\nu = \langle (\mathsf{H}_\mu - \mathsf{H}_\nu)\psi_\mu, \psi_\nu \rangle_\nu.$$

leads directly to corollary known as the integral Hellmann-Feynman theorem.

Corollary: If the conditions of the Hellmann-Feynman theorem are met, then

$$(\lambda_\mu - \lambda_\nu) = \frac{\langle (\mathsf{H}_\mu - \mathsf{H}_\nu)\psi_\mu, \psi_\nu \rangle_\nu}{\langle \psi_\mu, \psi_\nu \rangle_\nu}. \tag{3.1}$$

This result, also known as Parr's theorem, is useful for estimating molecular bond energies [32].

3.3 Adiabatic, Virial and Hypervirial Theorems

The adiabatic theorem states that the evolving eigenstate of a slowly varying Hamiltonian closely approximates at each instant the eigenstate that would exist if the Hamiltonian were at that point unvarying. A slowly varying Hamiltonian is dependent on a time-parameter so the Hellmann-Feynmann theorem can be applied. The work of Born and Fock [2], previously cited as containing a precursor of the Hellmann-Feynman theorem, is acknowledged as a significant proof of the adiabatic theorem. The histories of the two theorems involve many of the same people. A recent work by Joseph E.Avron and Alexander Elgart [1] is an excellent source of the history as well as providing the latest advance.

The virial theorem dates from the nineteenth century work of Rudolf Clausius. It states that for a bound system governed by an inverse square law of attraction average kinetic has half the magnitude of the average potential energy (taken to be zero at infinite separation). It is said that the Hellmann-Feynman theorem can be used to provide an alternate proof of the virial theorem. Allied theorems, as a group called hypervirial theorems, sometimes parallel or coincide with variant forms of the Hellmann-Feynman theorem [8].

Allied to the Hellmann-Feynmann theorem, in the class of hypervirial theorems, there exists an off-diagonal Hellmann-Feynman formula for the case of distinct eigenvalues, λ_m and λ_n, of the operator at a single value of the parameter ν,

$$(\lambda_m - \lambda_n) \left\langle \psi_n, \frac{\partial \psi_m}{\partial \nu} \right\rangle = \left\langle \psi_n, \frac{\partial \mathsf{H}}{\partial \nu} \psi_m \right\rangle,$$

where ψ_m and ψ_n are eigenfunctions associated with the respective eigenvalues. A simple derivation of the off-diagonal formula starts with

$$\lambda_m \psi_m = \mathsf{H} \psi_m.$$

Take the inner product with ψ_n and differentiate.

$$\frac{\partial}{\partial \nu} \langle \psi_n, \lambda_m \psi_m \rangle = \frac{\partial}{\partial \nu} \langle \psi_n, \mathsf{H} \psi_m \rangle .$$

Provided that we can take the differentiation inside the inner product and that $\left\langle \psi_n, \mathsf{H} \frac{\partial \psi_m}{\partial \nu} \right\rangle$ and $\left\langle \mathsf{H} \frac{\partial \psi_m}{\partial \nu}, \psi_n \right\rangle$ make sense, we proceed,

$$\frac{\partial \lambda_m}{\partial \nu} \langle \psi_n, \psi_m \rangle + \lambda_m \left\langle \psi_n, \frac{\partial \psi_m}{\partial \nu} \right\rangle + \lambda_m \left\langle \frac{\partial \psi_n}{\partial \nu}, \psi_m \right\rangle$$

$$= \left\langle \frac{\partial \psi_n}{\partial \nu}, \mathsf{H} \psi_m \right\rangle + \left\langle \mathsf{H} \psi_n, \frac{\partial \psi_m}{\partial \nu} \right\rangle + \left\langle \psi_n, \frac{\partial \mathsf{H}}{\partial \nu} \psi_m \right\rangle ,$$

where we have used the symmetry of the operator. Noting that the first term on the left side is zero by the orthogonality of the eigenfunctions and that the last term on the left side equals the first term on the right side, we simplify to the result,

$$(\lambda_m - \lambda_n) \left\langle \psi_n, \frac{\partial \psi_m}{\partial \nu} \right\rangle = \left\langle \psi_n, \frac{\partial \mathsf{H}}{\partial \nu} \psi_m \right\rangle .$$

This off-diagonal formula appears in the 1928 paper by Born and Fock [2] and is the Hellmann-Feynman antecedent previously mentioned, see example (c) in figure 1.1. Conditions under which this formula is said to hold are variously stated [5] [28] [9].

Chapter 4

The Variation of Zeros of Orthogonal Polynomials

In 1977, a physicist, John T. Lewis, in collaboration with a mathematician, Martin E. Muldoon, published a demonstration of the applicability of the Hellmann-Feynman theorem to a Sturm-Liouville operator and utilized the result to reveal monotonicity and convexity properties of the zeros of Bessel functions. Other mathematicians followed the lead in applying the theorem to the study of special functions and orthogonal polynomials. By 1988 a new technique of constructing tridiagonal matrix operators from three term recursion relations had come into use.

4.1 Sturm-Liouville Operators

Lewis and Muldoon [29] stated and proved, as a lemma, an adaptation of the Hellmann-Feynman theorem for the Sturm-Liouville problem,

$$\left[-\frac{d}{dx}\left(p(x)\frac{d}{dx}\right)+\nu^2 q(x)\right]\psi(x)=\lambda\phi(x)\psi(x), \qquad a<x\leq b,$$

with boundary conditions

$$\lim_{x\to a^+} p(x)\psi(x)\psi'(x) = p(b)\psi(b)\psi'(b).$$

They used integral notation, normalizing ψ with the inner product

$$\langle\psi,\psi\rangle := \int_a^b \phi\psi\overline{\psi}dx = \|\psi\|^2 = 1.$$

The parameter dependent operator,

$$\mathsf{L}_\nu := \frac{1}{\phi}\left[-\frac{d}{dx}\left(p\frac{d}{dx}\right) + \nu^2 q\right]$$

is symmetric for the given boundary conditions and inner product. Now, comparing the effect of two values of the parameter, μ and ν, on the inner product $\langle\psi_\mu,\psi_\nu\rangle$ we find

$$\langle\psi_\mu,(\mathsf{L}_\nu-\mathsf{L}_\mu)\psi_\nu\rangle = (\lambda_\nu-\lambda_\mu)\langle\psi_\mu,\psi_\nu\rangle = (\nu^2-\mu^2)\int_a^b q\psi_\mu\overline{\psi}_\nu dx$$

where we have dropped terms that integrate to zero. After dividing by $\nu-\mu$, the limit, $\mu\to\nu$, yields the derivative,

$$\frac{d\lambda_\nu}{d\nu} = \left\langle\psi_\nu, \frac{d\mathsf{L}_\nu}{d\nu}\psi_\nu\right\rangle = 2\nu\int_a^b q\psi_\nu\overline{\psi}_\nu dx,$$

which is the Hellmann-Feynman result.

Using the above result to rewrite the derivative $\frac{d}{d\nu}\frac{\lambda_\nu}{\nu}$, Lewis and Muldoon found,

$$\frac{d}{d\nu}\frac{\lambda_\nu}{\nu} = \frac{1}{\nu}\frac{d\lambda_\nu}{d\nu} - \frac{\lambda_\nu}{\nu^2} = 2\int_a^b q\psi_\nu\overline{\psi}_\nu dx - \frac{\lambda_\nu}{\nu^2} = \int_a^b\left[2q - \frac{\lambda_\nu\phi}{\nu^2}\right]\psi_\nu\overline{\psi}_\nu dx$$

where in the last step the normalization has been used. Then applying that result to the

rewriting of $\frac{d}{d\nu}\frac{\lambda_\nu}{\nu^2}$ they obtained,

$$\begin{aligned}
\frac{d}{d\nu}\frac{\lambda_\nu}{\nu^2} &= \frac{1}{\nu}\int_a^b \left[2q - \frac{\lambda_\nu \phi}{\nu^2}\right] \psi_\nu \overline{\psi}_\nu dx - \frac{\lambda_\nu}{\nu^3}\int_a^b \phi \psi_\nu \overline{\psi}_\nu dx \\
&= \frac{-2}{\nu^3}\int_a^b \left[-\nu^2 q dx + \lambda_\nu \phi\right] \psi_\nu \overline{\psi}_\nu dx \\
&= -\frac{2}{\nu^3}\int_a^b \psi_\nu \left[-\frac{d}{dx}\left(p(x)\frac{d\overline{\psi}_\nu}{dx}\right)\right] dx \\
&= -\frac{2}{\nu^3}\int_a^b p\left(\frac{d\psi_\nu}{d\nu}\right)\left(\frac{d\overline{\psi}_\nu}{d\nu}\right) dx
\end{aligned}$$

In the last steps they substitute from the original equation, integrate by parts and drop a term that evaluates to zero by reason of the boundary conditions.

4.2 A Second Derivative Version

A second derivative version of the Hellmann-Feynman theorem appeared in an article by Ismail and Muldoon [25].

First differentiate $\lambda_\nu \psi_\nu = \mathsf{L}_\nu \psi_\nu$ to obtain,

$$\frac{\partial \mathsf{L}_\nu}{\partial \nu}\psi_\nu = (\lambda_\nu - \mathsf{L}_\nu)\left(\frac{\partial \psi_\nu}{\partial \nu}\right) + \left(\frac{\partial \lambda_\nu}{\partial \nu}\right)\psi_\nu \tag{4.1}$$

If the definition of the inner product is independent of ν and ν is real, then the symmetry of the operator L_ν is inherited by its derivative, $\frac{\partial \mathsf{L}_\nu}{\partial \nu}$. Using this in differentiating

$$\frac{\partial \lambda_\nu}{\partial \nu} = \left\langle \psi_\nu, \frac{\partial \mathsf{L}_\nu}{\partial \nu}\psi_\nu \right\rangle$$

one obtains

$$\frac{\partial^2 \lambda_\nu}{\partial \nu^2} = \left\langle \psi_\nu, \frac{\partial^2 \mathsf{L}_\nu}{\partial \nu^2}\psi_\nu \right\rangle + \left\langle \frac{\partial \psi_\nu}{\partial \nu}, \frac{\partial \mathsf{L}_\nu}{\partial \nu}\psi_\nu \right\rangle + \left\langle \frac{\partial \mathsf{L}_\nu}{\partial \nu}\psi_\nu, \frac{\partial \psi_\nu}{\partial \nu} \right\rangle$$

Substituting for $\frac{\partial \mathsf{L}_\nu}{\partial \nu}\psi_\nu$ from 4.1 the rightmost two terms become

$$\left\langle \frac{\partial \psi_\nu}{\partial \nu}, (\lambda_\nu - \mathsf{L}_\nu)\frac{\partial \psi_\nu}{\partial \nu} + \frac{\partial \lambda_\nu}{\partial \nu}\psi_\nu \right\rangle + \left\langle (\lambda_\nu - \mathsf{L}_\nu)\frac{\partial \psi_\nu}{\partial \nu} + \frac{\partial \lambda_\nu}{\partial \nu}\psi_\nu, \frac{\partial \psi_\nu}{\partial \nu} \right\rangle$$

$$= \left\langle \frac{\partial \psi_\nu}{\partial \nu}, (\lambda_\nu - \mathsf{L}_\nu)\frac{\partial \psi_\nu}{\partial \nu} \right\rangle + \left\langle (\lambda_\nu - \mathsf{L}_\nu)\frac{\partial \psi_\nu}{\partial \nu}, \frac{\partial \psi_\nu}{\partial \nu} \right\rangle + \frac{\partial \lambda_\nu}{\partial \nu}\left(\left\langle \frac{\partial \psi_\nu}{\partial \nu}, \psi_\nu \right\rangle + \left\langle \psi_\nu, \frac{\partial \psi_\nu}{\partial \nu} \right\rangle \right)$$

Utilizing the hermiticity of $(\lambda_\nu - \mathsf{L}_\nu)$ and the normalization of ψ_ν we simplify to the result

$$\frac{\partial^2 \lambda_\nu}{\partial \nu^2} = \left\langle \psi_\nu, \frac{\partial^2 \mathsf{L}_\nu}{\partial \nu^2}\psi_\nu \right\rangle + 2\left\langle (\lambda_\nu - \mathsf{L}_\nu)\frac{\partial \psi_\nu}{\partial \nu}, \frac{\partial \psi_\nu}{\partial \nu} \right\rangle$$

This second derivative formula had appeared previously in the literature of quantum chemistry [6]. The second derivative formula depends on stronger assumptions than the first derivative formula; namely, differentiability of ψ_ν and boundedness of $\langle \frac{\partial \psi_\nu}{\partial \nu}, \frac{\partial \psi_\nu}{\partial \nu} \rangle$.

The following section relates to another innovation in the Ismail-Muldoon article.

4.3 Tridiagonal Matrices

The article by Ismail and Muldoon [25] and a second article, by Ismail [23], that appeared the previous year, describe a technique in the study of variation with respect to a parameter of zeros of orthogonal polynomials. The technique brings together three-term recurrence relations, tri-diagonal matrices and the Hellmann-Feynman theorem.

Let us examine some properties of tridiagonal matrices. Let A_N be an $N \times N$ tridiagonal matrix.

$$\mathsf{A}_N = \begin{pmatrix} b_0 & a_0 & & & & 0 \\ c_1 & b_1 & a_1 & & & \\ & c_2 & b_2 & \ddots & & \\ & & \ddots & \ddots & a_{N-3} & \\ & & & c_{N-2} & b_{N-2} & a_{N-2} \\ 0 & & & & c_{N-1} & b_{N-1} \end{pmatrix}$$

An inner product with respect to which A_N is hermitian must be a weighted inner product, $\langle \alpha, \beta \rangle = \sum_{i=0}^{N-1} \alpha_i \beta_i / \xi_i$, with ξ_i such that $a_i/\xi_i = c_{i+1}/\xi_{i+1}$, whence $\xi_{i+1} = \xi_i c_{i+1}/a_i$. So we define $\xi_0 := 1, \quad \xi_n := \prod_{i=1}^{n} c_i/a_{i-1}$.

For $N > 2$, the characteristic polynomial, $P_N(\lambda)$, takes the form,

$$P_N(\lambda) = (b_{N-1} - \lambda) P_{N-1}(\lambda) - a_{N-2} c_{N-1} P_{N-2}(\lambda), \tag{4.2}$$

while $\quad P_1(\lambda) = b_0 - \lambda \quad$ and $\quad P_2(\lambda) = (b_1 - \lambda) P_1(\lambda) - a_0 c_1$.

Now consider a sequence of polynomials. If a sequence of polynomials $\{Q_n(x)\}$ satisfies a three-term recurrence relation

$$x Q_n(x) = a_n Q_{n+1}(x) + b_n Q_n(x) + c_n Q_{n-1}(x) \tag{4.3}$$

$$Q_0(x) = 1, \quad Q_1(x) = (x - b_0)/a_0, \text{ and } \quad a_{n-1} c_n > 0, \quad n = 1, 2, \ldots$$

then there is a probability measure, $d\mu$, with infinite support and finite moments such that

$$\int_{-\infty}^{\infty} Q_n(x) Q_m(x) d\mu(x) = \xi_n \delta_{m,n}, \qquad \xi_0 := 1, \quad \xi_n := \prod_{i=1}^{n} c_i/a_{i-1}$$

If one constructs an $N \times N$ tridiagonal matrix, A_N, using the coefficients of the recurrence relation as elements, as done in anticipation above, then the characteristic polynomial, $P_N(\lambda)$ from (4.2), will be a multiple of $Q_N(\lambda)$, specifically,

$$P_N(\lambda) = Q_N(\lambda) \prod_{i=0}^{N-1} (-a_i).$$

Moreover, for λ a zero of Q_N, the vector $\mathcal{Q} := \{Q_0(\lambda), Q_1(\lambda), \ldots, Q_{N-1}(\lambda)\}$ is the associated eigenvector of A_N as revealed by using (4.3) to simplify the product $\mathsf{A}_N \mathcal{Q}$. Now, if the coefficients of the recurrence relation are differentiable functions of a parameter, ν, we can

apply the Hellmann-Feynman theorem and find,

$$\frac{d\lambda}{d\nu} = \left\langle \left(\frac{d}{d\nu} \mathsf{A}_N \right) \mathcal{Q}, \mathcal{Q} \right\rangle_\nu / \langle \mathcal{Q}, \mathcal{Q} \rangle_\nu, \tag{4.4}$$

where the indicated derivative is taken element wise. Importantly, this result does not require differentiation of the eigenvector or the orthogonal polynomials.

This version of the Hellmann-Feynman theorem together with certain other easily discerned properties of the system of orthogonal polynomials makes a variety of inferences possible. For example, birth and death process polynomials obey a recurrence relationship with coefficients related by $b_n = -(a_n + c_n)$, $a_n > 0$, and $c_n \geq 0$ for $n \geq 0$, with $c_n = 0$ only for $n = 0$, the lead coefficient of Q_n has the sign $(-1)^n$, and the zeros of Q_n lie between zero and the largest zero Λ of Q_N, $n < N$. Applying (4.4),

$$\frac{d\Lambda}{d\nu} \sum_{i=0}^{N-1} Q_i^2(\Lambda)/\xi_i = \sum_{i=0}^{N-1} Q_i(\Lambda)[-\frac{da_i}{d\nu} Q_{i+1}(\Lambda) - \frac{dc_i}{d\nu} Q_{i-1}(\Lambda) + \frac{d(a_i + c_i)}{d\nu} Q_i(\Lambda)]/\xi_i,$$

reveals a correlation of variation of Λ and the variation of the coefficients. If the coefficients a_n and c_n are nonincreasing (nondecreasing) functions of ν, then so is Λ, the largest zero of Q_N (for any choice of N.)

Analogous results are found for least zeros, and for other types of orthogonal polynomials, e. g. random walk polynomials. The paper by Ismail and Muldoon addresses infinite dimensional matrix cases.

Chapter 5

Generalized Eigenvalue Problems

In the generalized eigenvalue problem two operators separately transforming the same vector (function) yield vectors (functions) that differ from one another only by a scalar multiple,

$$\mathsf{A}x = \lambda \mathsf{M}x.$$

The scalar multiple, λ, is called a generalized eigenvalue of the operator pair. In the matrix operator context, λ satisfies the equation

$$\det(\mathsf{A} - \lambda\mathsf{M}) = \begin{vmatrix} a_{1,1} - \lambda m_{1,1} & a_{1,2} - \lambda m_{1,2} & \cdot & a_{1,n} - \lambda m_{1,n} \\ a_{2,1} - \lambda m_{2,1} & a_{2,2} - \lambda m_{2,2} & \cdot & a_{2,n} - \lambda m_{2,n} \\ \cdot & \cdot & \cdot & \cdot \\ a_{n,1} - \lambda m_{n,1} & a_{n,2} - \lambda m_{n,2} & \cdot & a_{n,n} - \lambda m_{n,n} \end{vmatrix} = 0.$$

An interesting case in which we might encounter a generalized eigenvalue problem is a mechanical system with n degrees of freedom governed by the system of Lagrange equations

$$\frac{\partial T}{\partial y_k} - \frac{d}{dt}\frac{\partial T}{\partial \dot{y}_k} = \frac{\partial U}{\partial y_k}, \tag{5.1}$$

where T is kinetic energy and U is potential energy. Let us suppose we have a stable

equilibrium point, $\frac{\partial U}{\partial y_k} = 0$ at $y_1 = y_2 = \cdots = y_n = 0$, with U at a minimum. Since U is only defined to within an additive constant, we take $U = 0$ at the equilibrium point. Our interest is discovering the natural frequency of small oscillations about this equilibrium point. In general,

$$T = \sum_{j,k=1}^{n} a_{j,k}\dot{y}_j\dot{y}_k \tag{5.2}$$

where the coefficients $a_{j,k}$ might be functions of the coordinates y, but we can regard them as constant for small oscillations. If we expand U in powers of the y, the first two terms are zero and our series begins with the second degree term. For small oscillations we neglect higher order terms and write

$$U = \sum_{j,k=1}^{n} b_{j,k}y_j y_k \tag{5.3}$$

with the constant coefficients $b_{j,k} = \frac{\partial^2 U}{\partial y_j \partial y_k}$. Substituting (5.2) and (5.3) into our system of Lagrange equations (5.1), we now have,

$$\begin{aligned}
a_{1,1}\ddot{y}_1 + a_{1,2}\ddot{y}_2 + \cdots + a_{1,n}\ddot{y}_n + b_{1,1}y_1 + b_{1,1}y_1 + \cdots + b_{1,1}y_1 = 0 \\
a_{1,1}\ddot{y}_1 + a_{1,2}\ddot{y}_2 + \cdots + a_{1,n}\ddot{y}_n + b_{1,1}y_1 + b_{1,1}y_1 + \cdots + b_{1,1}y_1 = 0 \\
\vdots \\
a_{1,1}\ddot{y}_1 + a_{1,2}\ddot{y}_2 + \cdots + a_{1,n}\ddot{y}_n + b_{1,1}y_1 + b_{1,1}y_1 + \cdots + b_{1,1}y_1 = 0
\end{aligned} \tag{5.4}$$

The solution has the form of harmonic oscillations of fixed frequency and phase but different amplitudes.

$$y_k = A_k \cos(\lambda t + \omega) \tag{5.5}$$

Substituting (5.5) into (5.4) we see the generalized eigenvalue problem,

$$(b_{1,1} - \lambda^2 a_{1,1})A_1 + (b_{1,2} - \lambda^2 a_{1,2})A_2 + \cdots + (b_{1,n} - \lambda^2 a_{1,n})A_n = 0,$$

$$(b_{2,1} - \lambda^2 a_{2,1})A_1 + (b_{2,2} - \lambda^2 a_{2,2})A_2 + \cdots + (b_{2,n} - \lambda^2 a_{2,n})A_n = 0,$$

$$\vdots$$

$$(b_{n,1} - \lambda^2 a_{n,1})A_1 + (b_{n,2} - \lambda^2 a_{n,2})A_2 + \cdots + (b_{n,n} - \lambda^2 a_{n,n})A_n = 0.$$

Only for λ^2 that make the corresponding determinant vanish can we have nontrivial solutions for the A_k.

If the coefficients $a_{j,k}, b_{j,k}$ in the above example were to be dependent on a parameter, an analog of the Hellmann-Feynman theorem could reveal the effect of the parameter on the natural frequencies of the system.

A manuscript of M. E. H. Ismail [24] describes an adaptation of the Hellmann-Feynman theorem to the generalized eigenvalue problem. In the context of a Hilbert space, $\mathcal{X}$, with inner product $\langle \cdot, \cdot \rangle$, let A and M be linear operators with M being a positive operator, that is $\langle \mathsf{M}x, x \rangle > 0$, for all $x \in \mathcal{X}$ with $\|x\| \neq 0$. We consider solutions of the generalized eigenvalue problem.

We begin by establishing a lemma, (asterisk denotes the adjoint).

LEMMA: Assume that $\mathsf{A}^*\mathsf{M} = \mathsf{M}^*\mathsf{A}$. Then the generalized eigenvalues are all real.

PROOF: We have

$$\lambda \langle \mathsf{M}x, \mathsf{M}x \rangle = \langle \mathsf{A}x, \mathsf{M}x \rangle = \langle x, \mathsf{A}^*\mathsf{M}x \rangle = \langle x, \mathsf{M}^*\mathsf{A}x \rangle = \langle \mathsf{M}x, \lambda \mathsf{M}x \rangle = \overline{\lambda} \langle \mathsf{M}x, \mathsf{M}x \rangle$$

Hence $\lambda = \overline{\lambda}$. □

We now come to Ismail's extension of the Hellmann-Feynman theorem to generalized eigenvalues.

THEOREM: Assume that A and M are two linear operators depending on a parameter ν, and $\nu \in I$ where I is an open interval. Assume further that M is a positive operator for all $\nu \in I$ and that $\mathsf{A}^*\mathsf{M} = \mathsf{M}^*\mathsf{A}$ holds on I. Let $\lambda = \lambda_\nu$ be a generalized eigenvalue with a generalized

eigenvector $x(\nu)$. Then

$$\frac{d\lambda_\nu}{d\nu} = \frac{\left\langle \left[\mathsf{M}^* \frac{d\mathsf{A}}{d\nu} - \mathsf{A}^* \frac{d\mathsf{M}}{d\nu} \right] x, x \right\rangle}{\langle \mathsf{M}x, \mathsf{M}x \rangle} \tag{5.6}$$

PROOF: Normalize x by

$$\langle \mathsf{M}x, \mathsf{M}x \rangle = 1$$

Clearly

$$\lambda_\nu = \langle \lambda_\nu \mathsf{M}x, \mathsf{M}x \rangle = \langle \mathsf{A}x, \mathsf{M}x \rangle \tag{5.7}$$

By differentiating the above equality we obtain

$$\begin{aligned} \frac{d\lambda_\nu}{d\nu} &= \left\langle \frac{d\mathsf{A}}{d\nu}x, \mathsf{M}x \right\rangle + \left\langle \mathsf{A}\frac{dx}{d\nu}, \mathsf{M}x \right\rangle + \left\langle \mathsf{A}x, \frac{d\mathsf{M}}{d\nu}x \right\rangle + \left\langle \mathsf{A}x, \mathsf{M}\frac{dx}{d\nu} \right\rangle \\ &= \left\langle \frac{d\mathsf{A}}{d\nu}x, \mathsf{M}x \right\rangle + \left\langle \frac{dx}{d\nu}, \mathsf{A}^*\mathsf{M}x \right\rangle + \left\langle \mathsf{A}x, \frac{d\mathsf{M}}{d\nu}x \right\rangle + \left\langle \mathsf{A}x, \mathsf{M}\frac{dx}{d\nu} \right\rangle \end{aligned}$$

Observe that the condition $\mathsf{A}^*\mathsf{M} = \mathsf{M}^*\mathsf{A}$ implies

$$\begin{aligned} \left\langle \frac{dx}{d\nu}, \mathsf{A}^*\mathsf{M}x \right\rangle + \left\langle \mathsf{A}x, \mathsf{M}\frac{dx}{d\nu} \right\rangle &= \left\langle \frac{dx}{d\nu}, \mathsf{M}^*\mathsf{A}x \right\rangle + \lambda \left\langle \mathsf{M}x, \mathsf{M}\frac{dx}{d\nu} \right\rangle \\ = \lambda \left[\left\langle \mathsf{M}\frac{dx}{d\nu}, \mathsf{M}x \right\rangle + \left\langle \mathsf{M}x, \mathsf{M}\frac{dx}{d\nu} \right\rangle \right] &= -\lambda \left[\left\langle \frac{d\mathsf{M}}{d\nu}x, \mathsf{M}x \right\rangle + \left\langle \mathsf{M}x, \frac{d\mathsf{M}}{d\nu}x \right\rangle \right] \end{aligned}$$

where the last step used the result of differentiating (5.7). Thus

$$\frac{d\lambda_\nu}{d\nu} = \left\langle \frac{d\mathsf{A}}{d\nu}x, \mathsf{M}x \right\rangle + \left\langle \frac{d\mathsf{M}}{d\nu}x, \mathsf{A}x \right\rangle$$

which simplifies to the right-hand side of (5.6). □

The requirement that $\mathsf{A}^*\mathsf{M} = \mathsf{M}^*\mathsf{A}$ is somewhat milder that requiring symmetry. Symmetry of both operators is sufficient to satisfy the condition.

Chapter 6

Conclusion

Although for some problems, particularly molecular force problems, $\langle \psi_\nu, \frac{\partial \mathsf{L}_\nu}{\partial \nu} \psi_\nu \rangle$, may not be simple to evaluate. Conceptually, the Hellmann-Feynman theorem is beautifully simple and direct and it has the capacity to reveal general properties of the variation of eigenvalues with respect to a parameter. However, it requires symmetry of the operator at the point where the derivative of the eigenvalue is taken. As seen in the tridiagonal matrix example, hermiticity at a point may possibly be achieved by specially crafting an inner product for the purpose. The cost in simplicity and directness becomes prohibitive for less tractable cases. It seems unlikely that completely general applicability can ever be achieved by a Hellmann-Feynman analog. However, a search for further extensions of applicability to special cases may yet be profitable.

The number of mathematicians who have taken an interest in the Hellmann-Feynman theorem remains small. The number of quantum chemists who take a mathematical interest in the theorem is also small. A few names recur frequently in searches for mathematically interesting works about the Hellmann-Feynman theorem.

Over the years, there have been researchers who used the theorem under other names, or unnamed, and who were perhaps unaware of the designation "Hellmann-Feynman theorem", for example, physicist Gregory Breit [4] writing on scattering theory, used two forms of

the theorem without name or attribution. Others who might be expected to be aware of the theorem seem not to have known of it by any name; *Perturbation Theory for Linear Operators* by Tosio Kato [27], for example, makes no mention of the theorem. Improving communication between disciplines might accelerate advances for all.

APPENDIX: ABOUT NOTATION

The purpose of this appendix is to aid the non-mathematician, but the mathematician unacquainted with Bra-Ket notation may find it helpful in the perusal of cited works from the field of quantum chemistry.

The inner product, or scalar product, $\langle \psi, \phi \rangle$ of complex n-vectors ψ and ϕ is defined

$$\langle \psi, \phi \rangle = \sum_{k=1}^{n} \psi_k \overline{\phi_k}$$

where $\overline{\phi_k}$ denotes the complex conjugate of ϕ_k.

This can be written as a matrix product by considering ψ and ϕ to be column vectors, then

$$\langle \psi, \phi \rangle = \psi^{\mathrm{T}} \overline{\phi}$$

Dirac Bra-Ket notation is a blending of matrix and inner product notations. A "Bra", $\langle \psi |$, is a row vector, the adjoint (conjugate transpose) of a "Ket", $| \psi \rangle$, column vector. Thus,

$$\langle \psi, \phi \rangle = \overline{\langle \psi | \phi \rangle} = \psi^{\mathrm{T}} \overline{\phi} = \psi \cdot \phi.$$

The inner product concept is more general than shown above. An integral may also define an inner product.

$$\langle \psi, \phi \rangle = \int \psi \overline{\phi} \omega d\tau$$

Where omega is a weighting function, which may be identically 1. If the weighting function or limits of integration depend on a parameter, ν, then the inner product itself is parameter dependent, $\langle \psi, \phi \rangle_\nu$. Sums also can have weighting as exemplified in the section on tridiagonal matrices.

CAUTION: In some older quantum literature, e. g. works of Pauli, the expression with parentheses rather than angle brackets, $(n|\mathsf{H}|m)$, denotes the element of matrix $\underline{\mathsf{H}}$ at row n, column m.

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