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Short Communication

Constraints and the Hellmann–Feynman Theorem

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It is pointed out that Hurley's condition applies even in the presence of Lagrange multipliers. Also a useful formula for $\partial E/\partial \sigma$ is derived which allows for the possibility that both the trial functions and the constraints may depend on σ.

Key words: Hellmann–Feynman – Constraints.

In 1954 Hurley [1] showed that if, in a variational calculation, the set of trial functions is invariant to changes in a parameter σ, then the optimal variational energies and trial functions will satisfy the Hellmann–Feynman theorem [2, 3] for σ. Recently however it has been claimed [4] that his discussion was not sufficiently general since it did not consider the possibility that the variational equations might involve Lagrange multipliers arising from constraints, for example orthogonality constraints, on the trial functions.

Our first purpose in this note is to show that this criticism of Hurley's discussion is unjustified. Our second purpose is to present a useful formula for the derivative of the optimal energy which generalizes the result found in [4] in that it applies whatever the set of trial functions and constraints.

Our first purpose is easily accomplished by noting that the use of Lagrange mutlipliers is, after all, only a convenience. In principle one can, without in any way changing the final results, by using the constraint equations, produce a set of trial functions which satisfies the constraints identically and evidently it is the latter set which is to be understood as "the set of trial functions" in Hurley's condition. In particular note that if the constraints don't involve σ, then this set will be independent of σ if the original set was.
Further, it may be well to emphasize the simplicity and generality of Hurley's condition since papers still keep appearing (for example see [5] and [6]) in which

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detailed proofs are given that certain variational approximations satisfy the Hellmann–Feynman theorem, proofs which are quite unnecessary since Hurley's condition is obviously satisfied. Also such detailed proofs can sometimes lead to errors (see for example footnote 11 of [7][1]).

Turning now to our second purpose, suppose that we have a set of trial functions involving numerical variational parameters A_i[2] and possibly the parameter σ, and suppose also that there are constraint equations

$$C_s(A, \sigma) = 0. \tag{1}$$

Since an optimal trial function will be of the form $\psi(A(\sigma), \sigma)$ where, as noted, the optimal variational parameters will in general depend on σ, then evidently we will have for the derivative of the optimal energy with respect to σ

$$\frac{\partial E}{\partial \sigma} = \left\langle \frac{\partial H}{\partial \sigma} \right\rangle + \sum_i \frac{\partial E}{\partial A_i}\frac{\partial A_i}{\partial \sigma} + \frac{\eth E}{\partial \sigma} \tag{2}$$

where $\langle \quad \rangle$ denotes expectation value (cf. $E = \langle H \rangle$) and where $\eth E/\partial \sigma$ represents the contribution arising from the explicit σ dependence of ψ and of any constraints which have been used in the evaluation of E. Generalizing the discussion in [4] we will now show that, in spite of appearance, it is unnecessary to calculate the $\partial A_i/\partial \sigma$.

We first note that the variational equations are

$$\frac{\partial E}{\partial A_i} = -\sum_s l_s \frac{\partial C_s}{\partial A_i} \tag{3}$$

where the l_s are Lagrange multipliers. However from (1) it follows that

$$\sum_i \frac{\partial C_s}{\partial A_i}\frac{\partial A_i}{\partial \sigma} + \frac{\eth C_s}{\partial \sigma} = 0 \tag{4}$$

which when combined with (3) yields

$$\sum_i \frac{\partial E}{\partial A_i}\frac{\partial A_i}{\partial \sigma} = \sum_s l_s \frac{\eth C_s}{\partial \sigma}. \tag{5}$$

Inserting this into (2) we then have as our final result

$$\frac{\partial E}{\partial \sigma} = \left\langle \frac{\partial H}{\partial \sigma} \right\rangle + \sum_s l_s \frac{\eth C_s}{\partial \sigma_i} + \frac{\eth E}{\partial \sigma}. \tag{6}$$

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[1] Unhappily this footnote has not been universally noted, and the original erroneous argument has been reproduced by Goodisman [8].

[2] For ease of exposition we allow numerical parameters only. However this, of course, implies no restriction in principle. More importantly, in our final result the nature of the A_i will be irrelevant.

References

1. Hurley, A. C.: Proc. Roy. Soc. (London) **A226**, 170 (1954)
2. Hellman, H.: Einführung in die Quantenchemie. Leipzig: Deuticke and Co. 1937
3. Feynman, R. P.: Phys. Rev. **56**, 340 (1939)
4. Pulay, P.: Modern theoretical chemistry, Vol. **4**, Schafer III, H. F. Ed. New York: Plenum Press 1977
5. Coulson, C. A.: Molec. Phys. **20**, 687 (1971)
6. Yurtsever, E., Hinze, J.: J. Chem. Phys. **71**, 1511 (1979)
7. Huo, W.: J. Chem. Phys. **49**, 1482 (1968)
8. Goodisman, J.: Diatomic interaction potential theory **2**. New York: Academic Press 1973

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