Perturbation expansion of variational principles at arbitrary order

Xavier Gonze
Unité de Physico-Chimie et de Physique des Matériaux,
Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium
(Received 12 December 1994)

When perturbation theory is applied to a quantity for which a variational principle holds (eigenenergies of Hamiltonians, Hartree-Fock or density-functional-theory energy, etc.), different variational-perturbation theorems can be derived. A general demonstration of the existence of variational principles for an even order of perturbation, when constraints are present, is provided here. Explicit formulas for these variational principles for even orders of perturbation, as well as for the "$2n+1$ theorem," to any order of perturbation, with or without constraints, are also exhibited. This approach is applied to the case of eigenenergies of quantum-mechanical Hamiltonians, studied previously by other methods.

PACS number(s): 31.15.−p, 02.30.Mv, 02.70.−c, 71.10.+x

I. INTRODUCTION

In an early study of the two-electron atomic systems, published in 1930, Hylleraas [1] observed that the knowledge of an eigenfunction and its first-order derivative with respect to some perturbation allows one to build easily not only the first derivative of its eigenenergy with respect to the same perturbation, but also its second and even third derivative. This result is one instance of a "$2n+1$ theorem," stated in this seminal paper: the $(2n+1)$-order derivative of the eigenenergies of some Hamiltonian can be calculated from the knowledge of the eigenfunction and its derivatives up to order n (see also Wigner [2]). In the same paper, Hylleraas also noticed that an expression for the second-order derivative of the eigenergy was variational (minimal) with respect to deviation of the first-order derivative of the wave function from its exact value.

Since that time, theoretical studies of physical systems submitted to small perturbations have been numerous. A large spectrum of perturbations such as small atomic displacements, electric fields, magnetic fields, small length scale changes, "transmutation" of elements, etc., eventually time dependent, have been considered, in the framework of widely used *ab initio* approaches such as the density-functional theory [3–7] (DFT), Hartree-Fock formalism [8–14], X_α approximation [15], multiconfiguration self-consistent field formalism (MCSCF) [9,14,16,17], configuration interaction technique [9,14,17], coupled-cluster [9,14] expansion, and also Moeller-Plesset expansion [9,13,14].

It is noticeable that a variational principle lies at the heart of most of these approaches. In that case, a nice interplay between a variational principle (or an extremal principle) and perturbation theory, found by Sinanoglu [18,19], allows one to find generalization of the Hylleraas results.

In order to situate the present work in the proper context, the second section will give a brief overview of arbitrary order perturbation expansion of variational principles. The interesting results obtained previously will be recalled. While the $2n+1$ has been demonstrated in the case of a variational principle under constraints, by Epstein [20], the existence of even-order variational principles in such a case has not been demonstrated. Also, the theorems have not been worked out up to the point where they give general, explicit expressions, in both cases with or without constraints.

In the third section, such explicit expressions will be provided for even-order variational principles, as well as for the $2n+1$ theorem, dealing with constraints through the Lagrange multiplier technique [20].

In a fourth section, these general expressions are applied to a quantum mechanical Hamiltonian, and results previously obtained from a mathematical approach, restricted to that case, are recovered.

II. BACKGROUND

In 1956, Dalgarno and Stewart [21] proposed an iterative procedure for building the $2n+1$ derivative of the eigenenergy of a quantum-mechanical Hamiltonian from only the knowledge of the derivatives of the eigenfunction up to order n, in the case of a change of a quantum mechanical Hamiltonian linear in the small perturbation parameter. This result was generalized later by Dupont-Bourdelet, Tillieu, and Guy [22] to Hamiltonians with a general dependence upon the small parameter. The latter authors gave *explicit* formulas for the $2n+1$ energy derivatives.

Taking a more general approach, Sinanoglu noticed that the very combination of *any* variational (or extremal) principle with perturbation theory will induce even-order variational (or extremal) principles [18]. Thus these results are not a characteristic feature of quantum mechanics, but could also appear in a classical context, or for any system in which a variational principle appears. The same approach leads also to the existence of a $2n+1$ theorem. As a consequence of this general interconnec-

tion, the formal structure of all perturbation-based methods of numerical calculation can be rather similar, as soon as they are derived from an extremal principle for the unperturbed quantity, whether it is the variational principle governing neutron diffusion [23], or the variational principle for normal modes (in classical mechanics) [24], the expectation value of a Hamiltonian, the Hartree-Fock energy obtained within a set of Slater determinants, Hohenberg and Kohn expression for the ground-state energy of a system within density-functional theory, different configuration interaction (CI) expressions of energy, etc.

Although the *existence* of the variation-perturbation theorems is easily proved, for a straight variational principle, by the rather elementary mathematical technique presented by Sinanoglu [18], this approach was never used to derive general, explicit, expressions. King and Komornicki [25] have built explicit expressions for the $2n+1$ theorem up to $n=2$, but did not pay attention to the variational property of even-order terms. Explicit expressions for the $2n+1$ theorem to any order have been derived by other, less powerful, mathematical techniques, on a case-by-case basis: for generic quantum mechanical Hamiltonians by Dupont-Bourdelet, Tillieu, and Guy [22,26], as mentioned before, but also for coupled-perturbed Hartree-Fock theory by Rebane [10,27], and for density-functional perturbation theory by Gonze and Vigneron [5,28]. Moreover, these techniques do not always generate even-order extremal principles.

In search of a general demonstration, Epstein noticed that the variational principle of the self-consistent field Hartree-Fock theory involved constraints, and that the Sinanoglu approach must be modified using a Lagrange multiplier technique [20]. He proved the $2n+1$ theorem for that case, but did not pay attention to the variational property of even-order expressions, and did not derive explicit formulas from his approach.

So, it seems that nothing has been done to prove even-order variational principles in the case of a constrained functional. Of course, it is formally possible to first map a variational principle under constraints to another variational principle without constraints, and from that other starting point, derive variational principles for even orders. But the explicit expressions derived from the transformed starting point could be much more involved, and likely useless (see Sec. IV, for an example). It is thus desirable to prove directly the even-order variational principles by using the Lagrange multiplier technique.

III. A VARIATIONAL APPROACH TO PERTURBATION THEORY

A. Definitions: Perturbation expansion, variational principle

Let us consider one perturbation, with one small parameter λ. Quantities such as the external potential, or the ground-state total energy of the system, are written as a perturbation series, as follows [for a generic quantity $X(\lambda)$]:

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \lambda^3 X^{(3)} + \cdots . \tag{1}$$

Note that the expansion coefficients are not the derivatives of $X(\lambda)$ with respect to λ, but are related to them by a simple numerical coefficient:

$$X^{(n)} = \frac{1}{n!} \frac{d^n X}{d\lambda^n}\bigg|_{\lambda=0} . \tag{2}$$

I consider now a general variational principle for E, a functional of Φ, and will call these quantities "energy" and "wave function," even if their actual area of application is completely unrelated to quantum mechanics [18,25].

In what follows, I will examine the consequences of a "variational principle" in the sense of a "lower variational bound" or "minimal principle": the difference between the value of the functional for a wave function slightly different than the "correct" one is *higher* than the value E_0 of the functional for that "correct" wave function Φ_0.

For a lower variational bound, under sufficient conditions of differentiability (always met in practice), the error in the functional is quadratic in the difference between wave functions, and is always positive: there exists some K such that

$$\forall \Phi, \quad 0 \leq E[\Phi] - E[\Phi_0] \leq K \|\Phi - \Phi_0\|^2 . \tag{3}$$

The subscript 0 indicates quantities found when the functional is at its extremal value.

The demonstrations that follow will apply, *mutatis mutandi*, for a "maximal principle" and also for a "stationary principle" (in which no extremal condition is met although the error on the functional is still quadratic—a saddle point—in the error on the wave function, see Appendix A).

For notational accuracy, I will distinguish between the functional $\hat{E}$ and the value that this functional can take, E.

B. Variational principle and perturbation theory: The case without constraint

Consider now that the functional $\hat{E}$ depends also on a parameter λ. The wave function that minimizes the functional will of course also depend on the parameter. It is possible, for λ in the neighborhood of zero, to define a fixed number K such that

$$\forall \Phi, \quad 0 \leq \hat{E}_{(\lambda)}[\Phi] - E_0(\lambda) \leq K \|\Phi - \Phi_0(\lambda)\|^2 , \tag{4}$$

with

$$E_0(\lambda) = \hat{E}_{(\lambda)}[\Phi_0(\lambda)] . \tag{5}$$

After some manipulation [18,19,28,29] one finds (see Appendix B)

$$E_0^{(2n+1)} = \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(2n+1)} \tag{6}$$

and [18,19]

$$E_0^{(2n)} = \min_{\delta\Phi_t} \left\{ \left(\hat{E}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right)^{(2n)} \right\} . \quad (7)$$

Equation (6) is the $2n+1$ theorem (the knowledge of the wave function up to order n gives the energy at order $2n+1$), while Eq. (7) describes the variational (extremal) property of even-order terms in the perturbation expansion: at the minimum, $\delta\Phi_t$ (the trial nth-order wave function) is equal to $\Phi_0^{(n)}$.

At this stage, it is possible to go further and obtain more explicit formulas from Eqs. (6) and (7). For this purpose, the domain of definition of the wave function is considered explicitly, so that one writes $\Phi(x)$, with x being a point in a many-dimensional space. Using m in place of either $2n$ or $2n+1$, one finds, after a few algebraic manipulations that involve Taylor series, as well as the definition Eq. (2),

$$\begin{aligned} E_0^{(m)} &= \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(m)} \\ &= \left\{ \hat{E}_{(\lambda)} \left[\Phi_0^{(0)} + \sum_{i=1}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(m)} \\ &= \sum_{k=0}^{m-1} \sum_{j=1}^{m-k} \int \cdots \int \frac{1}{j!k!} \sum_{i_1,\ldots,i_j=1}^{n} \delta(k+i_1+\cdots+i_j-m) \frac{\partial^{j+k}\hat{E}}{(\partial\lambda)^k \partial\Phi(x_1)\cdots\partial\Phi(x_j)} \\ &\quad \times \Phi^{(i_1)}(x_1)\cdots\Phi^{(i_j)}(x_j) dx_1 \cdots dx_j + \frac{1}{m!}\frac{\partial^m \hat{E}}{(\partial\lambda)^m} , \end{aligned} \quad (8)$$

where the derivatives of the functional $\hat{E}$ are evaluated at $\lambda=0$ and at the unperturbed wave function. Equation (8) gives a general *explicit* expression of the $2n+1$ theorem and the even-order variational principles, in the unconstrained case, when combined with Eqs. (6) and (7). This expression allows for further manipulations.

For example, it will simplify considerably if the number of derivatives of the functional $\hat{E}$ with respect to the wave functions that do not vanish is small. The index j in Eq. (8) will only run up to the largest value that gives nonzero derivatives. If the energy is a second-order polynomial in the wave function, j will only take the values of 1 or 2, and one is left with

$$\begin{aligned} E_0^{(m)} &= \sum_{k=0}^{m-2} \int\int \frac{1}{k!2} \sum_{i_1,i_2=1}^{n} \delta(k+i_1+i_2-m) \frac{\partial^{k+2}\hat{E}}{(\partial\lambda)^k \partial\Phi(x_1)\partial\Phi(x_2)} \Phi^{(i_1)}(x_1)\Phi^{(i_2)}(x_2) dx_1 dx_2 \\ &\quad + \sum_{k=0}^{m-1} \int \frac{1}{k!} \sum_{i_1=1}^{n} \delta(k+i_1-m) \frac{\partial^{k+1}\hat{E}}{(\partial\lambda)^k \partial\Phi(x_1)} \Phi^{(i_1)}(x_1) dx_1 + \frac{1}{m!}\frac{\partial^m \hat{E}}{(\partial\lambda)^m} . \end{aligned} \quad (9)$$

This case is the simplest possible one, since at least a quadratic dependency on the wave function is needed in order to have a variational principle.

Another simplification of Eq. (8) arises when the functional $\hat{E}$ is linear in the small parameter λ. Second- and higher-order derivatives of $\hat{E}$ with respect to λ will vanish, and one is left with

$$\begin{aligned} E_0^{(m)} &= \sum_{j=1}^{m-1} \int \ldots \int \frac{1}{j!} \sum_{i_1,\ldots,i_j=1}^{n} \delta(1+i_1+\cdots+i_j-m) \frac{\partial^{j+1}\hat{E}}{\partial\lambda\partial\Phi(x_1)\cdots\partial\Phi(x_j)} \Phi^{(i_1)}(x_1)\cdots \\ &\quad \times \Phi^{(i_j)}(x_j) dx_1 \cdots dx_j + \sum_{j=1}^{m} \int \cdots \int \frac{1}{j!} \sum_{i_1,\ldots,i_j=1} \delta(i_1+\cdots+i_j-m) \frac{\partial^j \hat{E}}{\partial\Phi(x_1)\cdots\partial\Phi(x_j)} \\ &\quad \times \Phi^{(i_1)}(x_1)\cdots\Phi^{(i_j)}(x_j) dx_1 \cdots dx_j + \left(\delta(m)\hat{E} + \delta(m-1)\frac{\partial\hat{E}}{\partial\lambda} \right) . \end{aligned} \quad (10)$$

C. The case with constraints

In order to minimize $\hat{E}[\Phi_t]$ under constraint, one defines (Lagrange multiplier method)

$$\hat{F}_\Lambda[\Phi_t] = \hat{E}[\Phi_t] - \Lambda\hat{C}[\Phi_t] , \quad (11)$$

where $\hat{C}[\Phi_t]$ is the functional that places a constraint on the domain of variation of Φ_t:

$$\hat{C}[\Phi_t] = 0 \ . \tag{12}$$

In Eq. (11), Λ is a Lagrange multiplier, chosen by the requirement that, after minimization, the solution Φ_t satisfies the constraint Eq. (12). This value of the Lagrange parameter is denoted by Λ_0. Note that for a wave function Φ_t that belongs to the allowed domain defined by Eq. (12), the values of the $\hat{F}$ and $\hat{E}$ functionals are identical.

In general, more than one constraint will be present simultaneously, but the line of thought presented here easily translates to this case, with only minor modifications (the number of Lagrange multipliers will be equal to the number of constraints). For ease of the presentation, only one constraint will be taken into account here.

In order to translate the method of demonstration of the variation-perturbation theorems that was used for the case without constraint to the case with constraints, one needs a variational principle within the Lagrange method, in replacement of Eq. (3). It can be found in Ref. [31]:

$\exists\Omega$ such that $\forall\Phi$,

$$0 \leq \hat{F}_{\Lambda_0}[\Phi] - \hat{F}_{\Lambda_0}[\Phi_0] + \Omega(\hat{C}[\Phi])^2 \leq K\|\Phi - \Phi_0(\lambda)\|^2 \ . \tag{13}$$

One can use Eq. (11) in order to rewrite Eq. (13) as follows:

$\exists\Omega$ such that $\forall\Phi$,

$$0 \leq \hat{E}[\Phi] - \Lambda_0\hat{C}[\Phi] + \Omega(\hat{C}[\Phi])^2 - E_0 \leq K\|\Phi - \Phi_0(\lambda)\|^2 \ . \tag{14}$$

Actually, it is similar to Eq. (3), but modified to include a constraint, considered up to second order.

The Lagrange method is now applied to the perturbation expansion of the constrained functional.

Equation (14) is valid for every λ. Note that the constraint could depend on λ. For the sake of generality, the possibility of this dependence is taken into account. Thus

$\exists\Omega$ such that $\forall\Phi$,

$$0 \leq \hat{E}_{(\lambda)}[\Phi] - \Lambda_0(\lambda)\hat{C}_{(\lambda)}[\Phi] + \Omega(\hat{C}_{(\lambda)}[\Phi])^2 - E_0(\lambda) \leq K\|\Phi - \Phi_0(\lambda)\|^2 \ . \tag{15}$$

Now, one follows the same path as for the unconstrained variational principle (Appendix B), and uses the trial function

$$\Phi = \sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1}\delta\Phi_t = \Phi_0(\lambda) - \lambda^{n+1}\left(\sum_{i=n+1}^{\infty} \lambda^{i-n-1}\Phi_0^{(i)} - \delta\Phi_t\right) \ , \tag{16}$$

equal to the exact one up to order n. The calculations leading to the variation-perturbation theorems are detailed in Appendix C. Modifications to the straight application of the unconstrained technique follow.

(1) One has to deal with the perturbation expansion of the constraint. It is shown in Appendix C that the expansion of the wave function up to order n fulfills the constraint also up to order n:

$$\left\{\hat{C}_{(\lambda)}\left[\sum_i^n \lambda^i \Phi_0^{(i)}\right]\right\}^{(n')} = 0 \quad \text{for } n' \leq n \ . \tag{17}$$

(2) Knowing the wave function up to order n, it is possible to calculate the perturbation expansion of the Lagrange multiplier $\Lambda_0(\lambda)$ up to order n. Indeed, the functional $\hat{F}_\Lambda[\Phi_t]$ must be a minimum, so its differential form must vanish, and the following condition is derived:

$$\forall\Delta\Phi_t, \quad \widehat{\delta E}_{(\lambda)}[\Delta\Phi_t]]_{\Phi_0(\lambda)} - \Lambda_0(\lambda)\widehat{\delta C}_{(\lambda)}[\Delta\Phi_t]]_{\Phi_0(\lambda)} = 0 \ . \tag{18}$$

The knowledge of the wave function up to order n will allow one to know the differentials $\widehat{\delta E}$ and $\widehat{\delta C}$ in Eq. (18) up to order n. As a consequence, $\Lambda_0(\lambda)$ will be known up to order n also.

The expression for the $2n+1$ theorems under constraint is

$$E_0^{(2n+1)} = \left\{\hat{F}_{(\lambda)}\left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)}\right]\right\}^{(2n+1)} = \left\{\hat{E}_{(\lambda)}\left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)}\right] - \Lambda_0(\lambda)\hat{C}_{(\lambda)}\left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)}\right]\right\}^{(2n+1)} \ , \tag{19}$$

which generalizes Eq. (6), and is a little more explicit than the expression found by Epstein [20].

One can also obtain the equivalent of the variational bound Eq. (7), but there is a supplementary constraint upon $\delta\Phi_t$ [expected from Eq. (17)]:

$$\left\{\hat{C}_{(\lambda)}\left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t\right]\right\}^{(n)} = 0 \ . \tag{20}$$

Namely, the trial order n wave function should fulfill the constraint up to order n. The variational bound is written as

$$0 \leq \left\{\hat{F}_{(\lambda)}\left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t\right]\right\}^{(2n)} - E_0^{(2n)} \leq K\|\Phi_0^{(n)} - \delta\Phi_t\|^2 \tag{21}$$

and one gets a new variational principle, under constraint,

$$E_0^{(2n)} = \min_{\delta\Phi} \left\{ \left(\hat{F}_{(\lambda)} \left[\sum_i^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right)^{(2n)} \right\} . \tag{22}$$

As in the unconstrained case, at the minimum, $\delta\Phi_t = \Phi_0^{(n)}$.

Thus the $2n+1$ theorem expressions include the Lagrange multiplier and its derivatives, as well as the constraint and its derivative, and the variational principles for even order are obtained under constraints.

Explicit expressions for Eqs. (19) and (20) are found from the following development (m stands for $2n$ or $2n+1$):

$$\begin{aligned} E_0^{(m)} = & \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(m)} - \sum_{l=0}^{m-(n+1)} \sum_{k=0}^{(m-l)-1} \sum_{j=1}^{(m-l)-k} \int \cdots \int \frac{1}{j!k!l!} \\ & \times \sum_{i_1,\ldots,i_j=1}^{n} \delta(k+i_1+\cdots+i_j-m+l) \frac{d^l\Lambda_0}{(d\lambda)^l} \frac{\partial^{j+k}\hat{C}}{(\partial\lambda)^k \partial\Phi(x_1)\cdot\partial\Phi(x_j)} \\ & \times \Phi^{(i_1)}(x_1)\cdots\Phi^{(i_j)}(x_j)dx_1\cdots dx_j - \sum_{l=0}^{m-(n+1)} \frac{1}{m!l!} \frac{d^l\Lambda_0}{(d\lambda)^l} \frac{\partial^{(m-l)}\hat{C}}{(\partial\lambda)^{(m-l)}} , \end{aligned} \tag{23}$$

where the first part of this expression was obtained in Eq. (8).

Equation (23) will become simpler if the constraint does not depend on the small parameter of the perturbation expansion, which is the case for most applications:

$$\begin{aligned} E_0^{(m)} = & \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(m)} - \sum_{l=0}^{m-(n+1)(m-l)} \sum_{j=1}^{(m-l)} \int \cdots \int \frac{1}{j!l!} \sum_{i_1,\ldots,i_j=1}^{n} \delta(i_1+\cdots+i_j-m+l) \\ & \times \frac{d^l\Lambda_0}{(d\lambda)^l} \frac{\partial^j\hat{C}}{\partial\Phi(x_1)\cdots\partial\Phi(x_j)} \Phi^{(i_1)}(x_1)\cdots\Phi^{(i_j)}(x_j)dx_1\cdots dx_j . \end{aligned} \tag{24}$$

Finally, if the constraint is moreover a second-order polynomial in the wave functions, one gets

$$\begin{aligned} E_0^{(m)} = & \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] \right\}^{(m)} - \sum_{l=0}^{m-(n+1)} \int \frac{1}{l!2} \sum_{i_1,i_2=1}^{n} \delta(i_1+i_2-m+l) \frac{d^l\Lambda_0}{(d\lambda)^l} \frac{\partial^2\hat{C}}{\partial\Phi(x_1)\partial\Phi(x_2)} \\ & \times \Phi^{(i_1)}(x_1)\Phi^{(i_2)}(x_2)dx_1dx_2 - \sum_{l=0}^{m-(n+1)} \int \frac{1}{l!} \sum_{i_1=1}^{n} \delta(i_1-m+l) \frac{d^l\Lambda_0}{(d\lambda)^l} \frac{\partial\hat{C}}{\partial\Phi(x_1)} \Phi^{(i_1)}(x_1)dx_1 . \end{aligned} \tag{25}$$

In this section, the existence of even-order variational principles under constraints has been proven to all orders, Eq. (22), and expressions more explicit than the published ones have been derived, Eqs. (8)–(10) and (23)–(25).

IV. APPLICATION TO A QUANTUM-MECHANICAL HAMILTONIAN

The quantum-mechanical variational principle (Ritz principle)

$$\forall\Phi_t \text{ normalized}, \quad E_0 \leq \langle\Phi_t|H|\Phi_t\rangle = \hat{E}[\Phi_t] \tag{26}$$

does *not* involve a "simple" quadratic functional of the wave functions, since the wave functions are constrained to be normalized. The normalization requirement is not mandatory in quantum mechanics, but if an unconstrained formulation is used,

$$\forall\Phi_t, \quad E_0 \leq \frac{\langle\Phi_t|H|\Phi_t\rangle}{\langle\Phi_t|\Phi_t\rangle} = \hat{E}[\Phi_t] , \tag{27}$$

the simplicity of the functional form is lost, and the expressions become much more involved (see Sec. IV C) [32].

The expression for the $2n+1$ theorem in the case of the quantum mechanical Hamiltonian, that was obtained in Ref. [5] by elementary means, will now be derived directly from the general formula of Sec. III, with the variational principle Eq. (26). Then I will compare this result with the lowest-order formulas obtained from the unconstrained formulation, Eq. (27), in order to show clearly the kind of simplifications that a constrained formulation allows. Other explicit expressions for the $2n+1$ theorem in the case of the quantum-mechanical Hamiltonian [21,22] used another normalization for the perturbation expansion of the wave function. The relation between the different normalizations is not difficult to establish, but will not be exposed here.

A. Variational principle for normalized wave functions

Before examining the perturbation expansion, one must apply the Lagrange method to the quantum mechanics variational principle.

In order to find the ground state, the energy functional

$$\hat{E}[\Phi_t] = \langle \Phi_t | H | \Phi_t \rangle \tag{28}$$

is to be minimized under the constraint

$$0 = \hat{C}[\Phi_t] = \langle \Phi_t | \Phi_t \rangle - 1 \ . \tag{29}$$

Together, they make the Lagrange functional

$$\hat{F}_\Lambda[\Phi_t] = \langle \Phi_t | H | \Phi_t \rangle - \Lambda[\langle \Phi_t | \Phi_t \rangle - 1] \ . \tag{30}$$

The minimum condition on Eq. (30) leads to

$$\forall \Delta\Phi_t, \quad 0 = (\langle \Delta\Phi_t | H | \Phi_0 \rangle - \Lambda \langle \Delta\Phi_t | \Phi_0 \rangle) + (\text{H.c.}) \tag{31}$$

[(H.c.) means Hermitian conjugate] or also

$$\forall \Delta\Phi_t, \quad 0 = 2\,\mathrm{Re}(\langle \Delta\Phi_t | H | \Phi_0 \rangle - \Lambda \langle \Delta\Phi_t | \Phi_0 \rangle) \ , \tag{32}$$

which means

$$0 = H|\Phi_0\rangle - \Lambda|\Phi_0\rangle \ . \tag{33}$$

Introducing the constraint Eq. (29), one finds an eigenvalue problem. The final premultiplication of Eq. (33) by $\langle \Phi_0 |$ and the use of Eqs. (28) and (29) lead to the identification of the Lagrange parameter with the eigenenergy E. Thus Eq. (33) is the Schrödinger equation (see Appendix A).

B. Perturbation expansion of the constrained variational principle

Because the energy Eq. (28) and constraint Eq. (29) are both second-order polynomials in the wave functions, and, moreover, because the constraint does not depend on the small parameters that affect the Hamiltonian, one can use the simplified expressions Eqs. (9) and (25) instead of Eqs. (8) and (23). This gives

$$\begin{aligned} E_0^{(m)} = & \sum_{k=0}^{m-2} \sum_{i_1,i_2=1}^{n} \delta(k+i_1+i_2-m) \langle \Phi^{(i_1)} | H^{(k)} | \Phi^{(i_2)} \rangle + \sum_{k=0}^{m-1} \sum_{i_1=1}^{n} \delta(k+i_1-m) \\ & \times (\langle \Phi^{(0)} | H^{(k)} | \Phi^{(i_1)} \rangle + \langle \Phi^{(i_1)} | H^{(k)} | \Phi^{(0)} \rangle) + \langle \Phi^{(0)} | H^{(m)} | \Phi^{(0)} \rangle \\ & - \sum_{l=0}^{m-(n+1)} \sum_{i_1,i_2=1}^{n} \delta(i_1+i_2-m+l) \Lambda_0^{(l)} \langle \Phi^{(i_1)} | \Phi^{(i_2)} \rangle \\ & - \sum_{l=0}^{m-(n+1)} \sum_{i_1=1}^{n} \delta(i_1-m+l) \Lambda_0^{(l)} (\langle \Phi^{(0)} | \Phi^{(i_1)} \rangle + \langle \Phi^{(i_1)} | \Phi^{(0)} \rangle) \ . \end{aligned} \tag{34}$$

And, after gathering the terms adequately

$$\begin{aligned} E_0^{(m)} = & \sum_{k=0}^{m} \sum_{i_1,i_2=0}^{n} \delta(k+i_1+i_2-m) \langle \Phi^{(i_1)} | H^{(k)} | \Phi^{(i_2)} \rangle \\ & - \sum_{l=0}^{m-(n+1)} \sum_{i_1,i_2=0}^{n} \delta(i_1+i_2-m+l) \\ & \times \Lambda_0^{(l)} \langle \Phi^{(i_1)} | \Phi^{(i_2)} \rangle \ . \end{aligned} \tag{35}$$

Because of the identification between the Lagrange multiplier and the energy, demonstrated in the preceding subsection, this result is equivalent to Eq. (A1) of Ref. [5]. The variational property of this equation for even orders of perturbation was unnoticed there.

Thus, starting from the general formulas Eqs. (8) and (23), it was shown how to derive the expressions for $2n+1$ and variational principles for a generic Hamiltonian that were obtained earlier by completely different means [21,22,5]. Of course, the technique that starts from general principles can be applied to a much wider set of problems (including Hartree-Fock and density-functional-theory variational principles) than these previous approaches.

C. Lowest-order formulas derived from the constrained and unconstrained variational principles

At the first and second order of perturbation, the *constrained* functional Eq. (26) gives the Hellmann-Feynman theorem [33]

$$E_\alpha^{(1)} = \langle \Phi_\alpha^{(0)} | H^{(1)} | \Phi_\alpha^{(0)} \rangle \tag{36}$$

and the Hylleraas variational principle [1] for the first-order wave function,

$$\begin{aligned} E_0^{(2)} & \le \hat{E}^{(2)}_{\text{constrained}}[\Phi_0^{(0)}, \Phi_{0,\text{trial}}^{(1)}] \\ & = \langle \Phi_{0,\text{trial}}^{(1)} | H^{(1)} | \Phi_0^{(0)} \rangle + \langle \Phi_{0,\text{trial}}^{(1)} | (H-E_0)^{(0)} | \Phi_{0,\text{trial}}^{(1)} \rangle \\ & \quad + \langle \Phi_0^{(0)} | H^{(2)} | \Phi_0^{(0)} \rangle + \langle \Phi_0^{(0)} | H^{(1)} | \Phi_{0,\text{trial}}^{(1)} \rangle \ , \end{aligned} \tag{37}$$

valid under the condition

$$\langle \Phi_0^{(0)} | \Phi_{0,\text{trial}}^{(1)} \rangle + \langle \Phi_{0,\text{trial}}^{(1)} | \Phi_0^{(0)} \rangle = 0 \ . \tag{38}$$

The first-order expression for the *unconstrained* functional Eq. (27), for $m=1$, $n=0$, derived from Eq. (8) gives

$$E_0^{(1)} = \frac{\langle \Phi_0^{(0)} | H^{(1)} | \Phi_0^{(0)} \rangle}{\langle \Phi_0^{(0)} | \Phi_0^{(0)} \rangle} , \tag{39}$$

which is reasonably simple, and reduces to Eq. (36),when normalized wave functions are considered.

By contrast, the second-order expression from Eqs. (8) and (27), for $m=2$, $n=1$, takes the form

$$\begin{aligned} E_0^{(2)} &\leq \hat{E}^{(2)}_{\text{unconstrained}}[\Phi_0^{(0)}, \Phi_{0,\text{trial}}^{(1)}] \\ &= \frac{1}{N^{(0)}} (\langle \Phi_0^{(0)} | H^{(1)} | \Phi_{0,\text{trial}}^{(1)} \rangle + \langle \Phi_{0,\text{trial}}^{(1)} | H^{(0)} | \Phi_{0,\text{trial}}^{(1)} \rangle \langle \Phi_0^{(0)} | H^{(2)} | \Phi_0^{(0)} \rangle \\ &\quad + \langle \Phi_{0,\text{trial}}^{(1)} | H^{(1)} | \Phi_0^{(0)} \rangle) - \frac{N^{(1)}}{(N^{(0)})^2} (\langle \Phi_0^{(0)} | H^{(0)} | \Phi_{0,\text{trial}}^{(1)} \rangle + \langle \Phi_0^{(0)} | H^{(1)} | \Phi_0^{(0)} \rangle \\ &\quad + \langle \Phi_{0,\text{trial}}^{(1)} | H^{(0)} | \Phi_0^{(0)} \rangle) - \frac{1}{(N^{(0)})^2} \left(\langle \Phi_{0,\text{trial}}^{(1)} | \Phi_{0,\text{trial}}^{(1)} \rangle + \frac{(N^{(1)})^2}{N^{(0)}} \right) \langle \Phi_0^{(0)} | H^{(0)} | \Phi_0^{(0)} \rangle , \end{aligned} \tag{40}$$

where

$$N^{(0)} = \langle \Phi_0^{(0)} | \Phi_0^{(0)} \rangle \tag{41}$$

and

$$N^{(1)} = \langle \Phi_0^{(0)} | \Phi_{0,\text{trial}}^{(1)} \rangle + \langle \Phi_{0,\text{trial}}^{(1)} | \Phi_0^{(0)} \rangle . \tag{42}$$

The functional Eq. (40) is extremal with respect to $\Phi_{0,\text{trial}}^{(1)}$, without constraint on the latter. Unfortunately, it is rather obscure, and difficult to handle. The simple normalization requirements $N^{(0)}=1$ and $N^{(1)}=0$ would allow recovery of Eq. (37).

Although the two approaches, constrained and nonconstrained, are equally valid, giving, respectively, Eqs. (37) and (40), the use of the normalization constraint gives much simpler expressions. This statement would become even stronger for higher orders of perturbation. By this example, the potential utility of the constrained approach is exhibited.

V. CONCLUSION AND PERSPECTIVES

In this paper, I have provided a general demonstration of the even-order variational (or extremal) principle in the constrained case (Sec. III). As a consequence, even-order variational principles for Hartree-Fock and DFT methods (among others) can be obtained in a constrained formulation, to all orders of perturbation. Explicit expressions for the variation-perturbation results are also given, both in the constrained and unconstrained cases. This approach is illustrated for the Ritz variational principle.

The approach presented here has already led to applications, in the form of a variational formulation of the density-functional perturbation theory, up to the third derivative of the energy [7,30]. For this density-functional perturbation theory, many constraints are present, since all the occupied Kohn-Sham wave functions have to be orthonormalized with respect to each other. Thus one obtains a set of Lagrange parameters. The generality of the present approach allows one to apply it to the perturbation expansion of arbitrary variational or extremal principles, in fields unrelated to quantum mechanics.

ACKNOWLEDGMENTS

It is a pleasure to thank D. C. Allan, J.-C. Charlier, Ph. Ghosez, C. Lee, K. Rabe, and G.-M. Rignanese for their encouragement and their interest in this work. I thank especially G.-M. Rignanese and Ph. Ghosez for carefully reading the lecture notes (UCL-PHYS 3915) on which this paper was mostly based. This paper was written in part at Cornell University (LASSP), during a stay made possible with the help of M. Teter and C. Umrigar. I also acknowledge financial support from FNRS-Belgium.

APPENDIX A: VARIATIONAL PRINCIPLE AND THE SCHRÖDINGER EQUATION: MINIMUM OR SADDLE POINTS

The Schrödinger equation (fulfilled by all the eigenstates) is not equivalent to the determination of a global minimum of the Ritz principle. Only the ground state fulfills a minimum principle. By contrast, the eigenenergies that do not correspond to the ground state are actually saddle points of the functional Eq. (30). For them there exists a stationarity requirement, but no extremal principle. So, if

$$\| \Phi_t - \Phi_\alpha \| = \eta \tag{A1}$$

is the error in the trial wave function of an excited state, then, for sufficiently small η,

$$\forall \Phi_t \text{ normalized}, \quad |\hat{E}[\Phi_t] - E_\alpha| \leq K \eta^2 , \tag{A2}$$

where K is a fixed number, independent of η.

This is to be contrasted with the variational bound (minimal principle) for the ground-state wave functions ($\alpha=0$):

$$\forall \Phi_t \text{ normalized}, \quad 0 \leq \hat{E}[\Phi_t] - E_0 \leq K \eta^2 . \tag{A3}$$

In both cases, there will exist a $2n+1$ theorem, but the

variational principle for even-order derivatives will either be a minimum principle (for the ground state) or only a stationary principle (for the excited states).

APPENDIX B: PERTURBATION EXPANSION OF AN UNCONSTRAINED VARIATIONAL PRINCIPLE

In order to investigate the connection between perturbation theory and the variational principle, one considers first the expansion of the exact wave function

$$\Phi_0(\lambda) = \sum_{i=0}^{\infty} \lambda^i \Phi_0^{(i)} , \tag{B1}$$

then the trial wave function

$$\Phi_t = \sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta\Phi_t$$

$$= \Phi_0(\lambda) - \lambda^{n+1} \left(\sum_{i=n+1}^{\infty} \lambda^{i-n-1} \Phi_0^{(i)} - \delta\Phi_t \right) . \tag{B2}$$

The latter is the exact one up to order n. Introducing Eq. (B2) into Eq. (4), and taking advantage of Eq. (B1), one gets

$$0 \le \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta\Phi_t \right] - E_0(\lambda)$$

$$\le K \lambda^{2n+2} \left\| \sum_{i=n+1}^{\infty} \lambda^{i-n-1} \Phi_0^{(i)} - \delta\Phi_t \right\|^2 , \tag{B3}$$

an equation that is valid for all $\delta\Phi_t$. If $\delta\Phi_t$ is chosen to be zero in Eq. (B3), one obtains

$$0 \le \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} \right] - E_0(\lambda)$$

$$\le K \lambda^{2n+2} \left\| \sum_{i=0}^{\infty} \lambda^i \Phi_0^{(i+n+1)} \right\|^2 , \tag{B4}$$

a result derived by Sinanoglu [18], although here written in a different form.

Thus the knowledge of the perturbation series of $\Phi_0(\lambda)$ up to (including) order n gives an error in the evaluation of the exact eigenenergy that is on the order of λ^{2n+2}.

Continuing to work on Eq. (B4), when only terms up to order $2n+1$ are considered, the quantity between the two inequality signs is zero. So, this expression simplifies to Eq. (6): the $(2n+1)$st term of the expansion of the energy in powers of λ is equal to the $(2n+1)$st term of the expansion of $\hat{E}_{(\lambda)}[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)}]$, a quantity that includes derivatives of the wave function up to order n only.

Now, one considers again Eq. (B3), but at order λ^{2n+2}. Because it is known that the expansion of the term between brackets, up to order $2n+1$, vanishes, one is left with

$$0 \le \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta\Phi_t \right] \right\}^{(2n+2)} - E_0^{(2n+2)}$$

$$\le K \| \Phi_0^{(n+1)} - \delta\Phi_t \|^2 . \tag{B5}$$

This is a variational bound for the $(2n+2)$-order derivative of the energy when the wave function is already known up to order n. Actually, because n is a dummy argument, one can shift n to $n-1$ and write [18]

$$0 \le \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right\}^{(2n)} - E_0^{(2n)}$$

$$\le K \| \Phi_0^{(n)} - \delta\Phi_t \|^2 . \tag{B6}$$

This expression can also be worked in a more compact form, to give Eq. (7).

APPENDIX C: DEMONSTRATION OF EQS. (19)–(21)

Starting from Eq. (15), one gets the following inequalities:

$$\exists \Omega \text{ such that } \forall \delta\Phi_t, \quad 0 \le \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta\Phi_t \right] - \Lambda_0(\lambda) \hat{C}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta\Phi_t \right]$$

$$+ \Omega \left(\hat{C}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \Phi_0^{(i)} | + \lambda^{n+1} \delta\Phi_t \right] \right)^2 - E_0(\lambda)$$

$$\le K \lambda^{2n+2} \left\| \sum_{i=n+1}^{\infty} \lambda^{i-n-1} \Phi_0^{(i)} + \delta\Phi_t \right\|^2 . \tag{C1}$$

Forcing $\delta\Phi_t$ to vanish in Eq. (C1) gives

$$0 \leq \hat{E}_{(\lambda)}\left[\sum_{i=0}^{n}\lambda^i\Phi_0^{(i)}\right] - \Lambda_0(\lambda)\hat{C}_{(\lambda)}\left[\sum_{i=0}^{n}\lambda^i\Phi_0^{(i)}\right]$$

$$+\Omega\left(\hat{C}_{(\lambda)}\left[\sum_{i=0}^{n}\lambda^i\Phi_0^{(i)}\right]\right)^2 - E_0(\lambda)$$

$$\leq K\lambda^{2n+2}\left\|\sum_{i=n+1}^{\infty}\lambda^{i-n-1}\Phi_0^{(i)}\right\|^2 . \qquad \text{(C2)}$$

The constraint has to be expanded in a perturbation series. Because

$$\hat{C}_{(\lambda)}[\Phi_0(\lambda)] = 0 , \qquad \text{(C3)}$$

one derives

$$\hat{C}_{(\lambda)}\left[\sum_{i=0}^{n}\lambda^i\Phi_0^{(i)}\right] = \hat{C}_{(\lambda)}\left[\Phi_0(\lambda) - \lambda^{n+1}\right.$$

$$\left.\times\sum_{i=n+1}^{\infty}\lambda^{i-n-1}\Phi_0^{(i)}\right] , \qquad \text{(C4)}$$

and a Taylor expansion of Eq. (C4), complemented by Eq. (C3), shows that the wave function up to order n fulfills the constraint also up to order n, as mentioned in Eq. (17).

The inequalities in Eq. (C2) are expanded up to order $2n+1$. The square of the constraint is zero up to that order, as well as the right member of the inequality, which gives Eqs. (19). In order to obtain Eq. (21) from Eq. (C1), the shift from n to $n+1$ is performed first, then the constraint Eq. (20) is imposed.

[1] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).

[2] E. Wigner, Math. Natur. Anz. (Budapest) **53**, 477 (1935). The $2n+1$ theorem for $n=1$ is also mentioned in P. M. Morse and H. Feschbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Tome II, p. 1120.

[3] M. J. Stott and E. Zaremba, Phys. Rev. A **21**, 12 (1980); A. Zangwill and P. Soven, *ibid.* **21**, 1561 (1980); G. D. Mahan, *ibid.* **22**, 1780 (1980); *Local Density Theory of Polarizability* (Plenum, New York, 1990).

[4] N. E. Zein, Fiz. Tverd. Tela (Leningrad) **26**, 3028 (1984) [Sov. Phys. Solid State **26**, 1825 (1984)]; S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987); Z. H. Levine and D. C. Allan, *ibid.* **63**, 1719 (1989); P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1990); A. A. Quong and M. R. Pederson, *ibid.* **46**, 12 906 (1992); A. A. Quong and A. G. Eguiluz, Phys. Rev. Lett. **70**, 3955 (1993); C.-Z. Wang, Rici Yu, and H. Krakauer, *ibid.* **72**, 368 (1994); S. Yu Savrasov, *ibid.* **69**, 2819 (1992), and references therein.

[5] X. Gonze and J.-P. Vigneron, Phys. Rev. B **39**, 13 120 (1989).

[6] S. K. Ghosh and B. M. Deb, J. Chem. Phys. **71**, 295 (1982); L. J. Bartolotti, *ibid.* **80**, 5687 (1984); J. Phys. Chem. **90**, 5518 (1986); K. D. Sen and L. J. Bartolotti, Phys. Rev. A **45**, 2076 (1992), and references therein.

[7] X. Gonze, D. C. Allan, and M. P. Teter, Phys. Rev. Lett. **68**, 3603 (1992).

[8] R. D. Amos and J. E. Rice, Comput. Phys. Rep. **10**, 147 (1989).

[9] S. Bratoz, Colloq. Int. CNRS **82**, 287 (1958); A. Dalgarno, Proc. R. Soc. London, Ser. A **25**, 282 (1959); R. McWeeny, Phys. Rev. **126**, 1028 (1961); P. W. Langhoff, J. D. Lyons, and R. P. Hurst, *ibid.* **148**, 18 (1966); J. Gerrat and I. M. Mills, J. Chem. Phys. **49**, 1719 (1968); R. Moccia, Chem. Phys. Lett. **5**, 265 (1970); P. Pulay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer (Plenum, New York, 1977), Vol. 4, Chap. 4, p. 153; C. E. Dykstra and P. G. Jasien, Chem. Phys. Lett. **109**, 388 (1984); R. J. Cave and E. R. Davidson, J. Chem. Phys. **89**, 6798 (1988); G. J. B. Hurst, M. Dupuis, and E. Clementi, *ibid.* **89**, 385 (1988); and references therein.

[10] T. K. Rebane, Opt. Spectrosc. (USSR) **19**, 179 (1965).

[11] R. Moccia, Chem. Phys. Lett. **5**, 260 (1970).

[12] T.-S. Nee, R. G. Parr, and R. J. Bartlett, J. Chem. Phys. **64**, 2216 (1976).

[13] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. Symp. **13**, 225 (1979).

[14] P. Jorgensen and J. Simons, J. Chem. Phys. **79**, 334 (1983); J. Simons and P. Jorgensen, *ibid.* **79**, 3599 (1983).

[15] R. Ahlberg and O. Goscinski, J. Phys. B **6**, 2254 (1973); **8**, 2149 (1975).

[16] M. Rerat, Int. J. Quantum Chem. **36**, 169 (1989); M. Rerat, M. Merawa, and C. Pouchan, Phys. Rev. A **46**, 5471 (1992).

[17] P. Pulay, J. Chem. Phys. **78**, 5043 (1983).

[18] O. Sinanoglu, J. Chem. Phys. **34**, 1237 (1961).

[19] See J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, *Advances in Quantum Chemistry* (Academic, New York, 1964), Vol. 1, pp. 267, 288, and 300.

[20] S. T. Epstein, Chem. Phys. Lett. **70**, 311 (1980).

[21] A. Dalgarno and A. L. Stewart, Proc. R. Soc. London, Ser. A **238**, 269 (1956).

[22] F. Dupont-Bourdelet, J. Tillieu, and J. Guy, J. Phys. Radium **21**, 776 (1960).

[23] M. D. Kostin and H. Brooks, J. Math. Phys. **5**, 1691 (1964).

[24] J. N. Silverman, J. Phys. A **16**, 3471 (1983).

[25] H. F. King and A. Komornicki, J. Chem. Phys. **84**, 5646 (1986).

[26] See also Refs. [28,5].

[27] See also Ref. [12].

[28] See also A. Dal Corso and F. Mauri, Phys. Rev. B **50**, 5756 (1994).

[29] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).

[30] X. Gonze, following paper, Phys. Rev. A **52**, 1096 (1995).

[31] W. T. Reid, in *Control Theory and the Calculus of Variations*, edited by A. V. Balakrishnan (Academic, New York, 1969), p. 385.

[32] Note that sometimes it is possible to find a transformation of the constrained variational principle such that another principle, unconstrained, is obtained, and gives the same minimum as the original one, although it differs from it elsewhere. See Ref. [31].

[33] H. Hellmann, *Einfuhrung in die Quantenchemie* (Deuticke, Leipzig, 1937), pp. 61 and 285; R. P. Feynman, Phys. Rev. **56**, 340 (1939).