

## Geometric Approximation in Perturbation Theory\*

O. Goscinski and E. Brändas

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

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Even if the terms in a perturbation expansion show geometric behavior only in exceptional cases, e.g., the Hartree-Fock hydrogen atom, the geometrical sum rule leads to remarkable numerical accuracy in a number of cases beyond the apparent prerequisites for its applicability. The rule is here derived by variational perturbation theory and it is seen that it holds, whenever the norm of the first-order wave function is negligible with respect to unity. In other cases it holds in a modified form.

### I. INTRODUCTION

In connection with first-order iteration procedures, the geometric construction for reaching the limit is a well-known tool. The first analysis goes back to Schröder in 1870<sup>1</sup> but the process is rediscovered from time to time. It has been found to be particularly useful in self-consistent-field procedures.<sup>1</sup>

Also in connection with perturbation theory the geometric construction may be useful, e.g., in solving  $E=f(E)$ . For a survey of the development see Löwdin.<sup>2</sup>

It is evident that the Brillouin-Wigner theory is based on a geometric progression in an operator, and one may then wonder whether a similar structure holds for the various terms in the expectation value. Considering the fact that if  $K$  is an arbitrary operator and  $\{\Phi_k\}$  is a complete set, one has

$$\begin{aligned} \langle \Phi_0 | K^2 | \Phi_0 \rangle &= \langle \Phi_0 | K | \Phi_0 \rangle^2 \\ &+ \sum_{n \neq 0} |\langle \Phi_0 | K | \Phi_n \rangle|^2, \end{aligned} \quad (1)$$

and one would anticipate that the quantities  $\langle \Phi_0 | K^i | \Phi_0 \rangle$ ,  $i=1, 2, \dots$  do not form a geometric series, except in the case when  $\langle \Phi_0 | K | \Phi_n \rangle = 0$ , for all  $n > 0$ , which of course does not hold in general. In the Brillouin-type theory we have  $K = V^{1/2} T_0 V^{1/2}$  and  $\Phi_0 = V^{1/2} \phi_0$ , and the Schrödinger-type theory is essentially based on  $K = -(-R_0)^{1/2} V' (-R_0)^{1/2}$  with  $\Phi_0 = (-R_0)^{1/2} V \phi_0$  and  $V' = V - V_{00}$ .<sup>2</sup> In spite of these results, it seems as if certain perturbation sums show a remarkable "geometric" structure.

Recently Schulman and Musher discussed a geometric approximation to polarizabilities, which was demonstrated by empirical means to be applicable to some many-electron atoms.<sup>3</sup> The technique was later used by Amos and Roberts to compute magnetic susceptibilities with equally satisfactory results.<sup>4</sup>

The nature of the approximation is to assume that successive orders in a perturbation expansion form a geometric series. The assumption was

verified explicitly for the double perturbation treatment of the hydrogen-atom dipole polarizability based on a Hartree-Fock  $H_0$ .<sup>3,5</sup> It led to a closed result for the sum of the series, but its range of validity remained to be determined, and it was not clear that it could be justified at all.

In this article we discuss the condition under which a "geometric" behavior can be expected and perhaps of more interest procedures which yield the same end result without such a stringent assumption about the individual orders. The use of geometric series to sum terms in a perturbation expansion was discussed and used extensively by Kelly.<sup>6</sup>

### II. THE HYDROGEN-ATOM POLARIZABILITY

The well-known result is, of course,

$$\alpha = - \left. \frac{\partial^2 E}{\partial \epsilon^2} \right|_{\epsilon=0} = 4.5 a_0^3, \quad (2)$$

where the polarizability  $\alpha$  is given in terms of the second derivative of the energy with respect to the strength of an external, uniform electric field. Kelly considered the approximate method of solution.

$$\alpha = \alpha_0 + \alpha_1 \lambda + \alpha_2 \lambda^2 + \dots, \quad (3)$$

where  $\alpha_0$  is the polarizability of the Hartree-Fock hydrogen atom, and by using the perturbation methods of the many-body theory obtained a geometric series which led to the result<sup>5</sup>

$$\alpha_0 [1 - \alpha_1/\alpha_0]^{-1} = 4.527 a_0^3.$$

Epstein and Johnson<sup>7</sup> computed the first three terms in (3), and Schulman and Musher<sup>3</sup> the first six terms. The considerations and equations that lead to (3) are well described by Schulman and Musher. We repeat them here for convenience.

The zeroth-order Hamiltonian is

$$H_0 = -\frac{1}{2} \nabla^2 - 1/r + V = h + V, \quad (4)$$

where  $V$  is the Hartree-Fock (H-F) operator.

$$V = \int dv' \psi_0(r') |r - r'|^{-1} (1 - P_{rr'}) \psi_0(r'). \quad (5)$$

The zeroth-order solution is the 1s hydrogen-atom wave function, and the total Hamiltonian is

$$H(\lambda, \epsilon) = H_0 + \epsilon z - \lambda V. \quad (6)$$

Usual considerations<sup>8</sup> lead us to seek solutions of the form (the case of physical interest is  $\lambda = 1$ )

$$\psi(\lambda, \epsilon) = \psi_0 + \lambda \psi_{1,0} + \epsilon \psi_{0,1} + \lambda \epsilon \psi_{1,1} + \dots \quad (7)$$

and

$$E(\lambda, \epsilon) = E_0 + \lambda E_{1,0} + \epsilon E_{0,1} + \lambda \epsilon E_{1,1} + \dots \quad (8)$$

Furthermore, one is interested in functions and energies of respectively first and second order in  $\epsilon$ , but of all orders in  $\lambda$ . The  $\alpha_i$  appearing in (3) turn out to be given by

$$\alpha_i = -2E_{i,2} = -2\langle \psi_0 | z | \psi_{i,1} \rangle, \quad (9)$$

where the function  $\psi_{i,1}$  satisfies the equations

$$(E_0 - H_0) \psi_{0,1} = z \psi_0, \quad (10)$$

$$(E_0 - H_0) \psi_{i,1} = -V \psi_{i-1,1}, \quad i > 0.$$

In particular it should be noticed that

$$\begin{aligned} \alpha_{2i+1} &= 2\langle \psi_{i,1} | V | \psi_{i,1} \rangle, \\ \alpha_{2i+2} &= 2\langle \psi_{i,1} | V | \psi_{i+1,1} \rangle. \end{aligned} \quad (11)$$

The solutions of (10) are given by

$$\psi_{i,1} = (-R_0 V)^i R_0 z \psi_0, \quad i = 0, 1, \dots, \quad (12)$$

where  $R_0$  is the reduced resolvent

$$R_0 = P(E_0 - PH_0P)^{-1}, \quad P = 1 - |\psi_0\rangle\langle\psi_0|. \quad (13)$$

It follows from (12) that

$$\sum_{i=0}^{\infty} \psi_{i,1} = (1 + R_0 V)^{-1} R_0 z \psi_0 \equiv \psi_1. \quad (14)$$

The function  $\psi_1$  satisfies the inhomogeneous equation

$$(E_0 - h) \psi_1 = z \psi_0, \quad (15)$$

which is indeed the equation characterizing the first-order correction to the wave function of a hydrogen atom in an external electric field of unit strength in the  $z$  direction.  $\psi_1$  is then the exact solution to the problem at hand given by

$$\psi_1 = \pi^{-1/2} (r + \frac{1}{2} r^2) \cos \vartheta e^{-r}. \quad (16)$$

It is apparent from Eqs. (12) and (14) that  $\psi_1$  is obtained as a geometric series involving the operator  $R_0 V$ . Schulman and Musher point out that this does not imply that the individual terms should order by order be related numerically, unless  $H_0$  were to have a spectrum with a *single* contributing

excited state<sup>3</sup> and this is right, of course. What is remarkable in this particular example is that the  $\psi_{i,1}$  do very nearly form a geometric series of functions. The question is why this is so, since  $H_0$  does *not* have a single contributing excited state. Secondly, why does this lead to a geometric series for the  $\alpha_i$ ? The last question leads us to ask why a closed formula for the geometric sum is so accurate, since the individual terms are approximately in a geometric progression. A plausible surmise, which we will try to substantiate in this article, is that the closed formula for the polarizability obtained by assuming that the individual terms in (3) have a constant ratio ( $\alpha_1/\alpha_0$ ),

$$\alpha \approx \alpha_0 [1 - (\alpha_1/\alpha_0)]^{-1}, \quad (17)$$

is a very good approximation even when the terms in (3) do *not* form a geometric series. A variation perturbation approach previously used by us in other connections furnishes the formal framework to prove this assertion.<sup>9,10</sup> It was shown that an upper bound to the total energy is given by the expression

$$E \leq E_0 + \epsilon_1 + \bar{\lambda} \epsilon_2, \quad (18)$$

where  $E_0$ ,  $\epsilon_1$ , and  $\epsilon_2$  are ordinary Rayleigh-Schrödinger perturbation energies. The parameter  $\bar{\lambda}$  in many cases<sup>9,10</sup> is well approximated by

$$\bar{\lambda} \approx [1 - (\epsilon_3/\epsilon_2)]^{-1}, \quad (19)$$

which leads to an expression for the correction to the zeroth- and first-order energy which in some sense involves contributions from all orders, yet is expressible in terms of  $\epsilon_2$  and  $\epsilon_3$  only:

$$\epsilon_2 [1 - (\epsilon_3/\epsilon_2)]^{-1}. \quad (20)$$

One could have obtained (20) by assuming, without grounds very likely, that  $\epsilon_{k+1}/\epsilon_k \approx \epsilon_3/\epsilon_2$ , yet (20) is quite a good approximation regardless of that assumption. Notice the resemblance of (17) and (20).

Let us study why in this particular example there is a geometric behavior. Consider the first equation in (12)

$$\psi_{0,1} = R_0 z \psi_0 \quad (21)$$

which corresponds to the inhomogeneous equation

$$(E_0 - H_0) \psi_{0,1} = z \psi_0. \quad (22)$$

An interesting fact about (22) is that, if one attempts to solve it by the usual technique of  $(Z)^{-1}$  expansions<sup>11</sup> the leading term satisfies (15). The zeroth-order solution of (22) in the sense of  $(Z)^{-1}$  expansions happens to be the function  $\psi_1$ , the exact solution of the problem. This is not surprising though unconventional. We may get better insight into this problem if we approximate  $R_0$  by an inner projection into a one-dimensional manifold spanned by<sup>12</sup>  $\psi_1$

$$R_0 \leq |\psi_1\rangle \langle \psi_1 | E_0 - H_0 | \psi_1 \rangle^{-1} \langle \psi_1 |. \quad (23)$$

Since  $\psi_1$  satisfies (15) the denominator in (23) is just

$$\begin{aligned} \langle \psi_1 | E_0 - h - V | \psi_1 \rangle &= \langle \psi_1 | z | \psi_0 \rangle - \langle \psi_1 | V | \psi_1 \rangle \\ &= -\frac{1}{2} \alpha - \langle \psi_1 | V | \psi_1 \rangle. \end{aligned} \quad (24)$$

This means, according to (21), (23), and (24), that

$$\begin{aligned} \psi_{0,1} &\approx -[\langle \psi_1 | z | \psi_0 \rangle / (\frac{1}{2} \alpha + \langle \psi_1 | V | \psi_1 \rangle)] \psi_1 \\ &= [\alpha / (\alpha + 2 \langle \psi_1 | V | \psi_1 \rangle)] \psi_1. \end{aligned} \quad (25)$$

In other words, if the usual perturbation treatment of inhomogeneous equations based upon  $(Z)^{-1}$  expansions is used as a choice for the approximation of the reduced resolvent  $R_0$  to be considered, one immediately sees that  $\psi_{0,1}$  is proportional to the exact solution  $\psi_1$ . In order to see how good this approximation is we just have to exploit the operator inequality (23). From (9), (21), (23), and (24) it follows that

$$\begin{aligned} \alpha_0 &= -2 \langle \psi_0 | z R_0 z | \psi_0 \rangle \\ &\leq 2 |\langle \psi_0 | z | \psi_1 \rangle|^2 / (\frac{1}{2} \alpha + \langle \psi_1 | V | \psi_1 \rangle) \\ &= [\alpha^2 / (\alpha + 2 \langle \psi_1 | V | \psi_1 \rangle)] = \tilde{\alpha}_0. \end{aligned} \quad (26)$$

In order to compare with the results of Schulman and Musher we write (25) in the form

$$\psi_{0,1} \approx (1-k) \psi_1, \quad 1-k = \alpha / (\alpha + 2 \langle \psi_1 | V | \psi_1 \rangle), \quad (27)$$

which implies  $\alpha_0 \leq \alpha(1-k)$ . (28)

Since a first-order wave function yields energies through third order, the approximate  $\psi_{0,1}$  of (27) allows us to construct the third-order quantity  $\tilde{\alpha}_1$ . From (9), (12), and (27)

$$\begin{aligned} \alpha_1 &= -2 \langle \psi_0 | z | \psi_{1,1} \rangle = 2 \langle \psi_0 | z R_0 V R_0 z | \psi_0 \rangle \\ &\approx \tilde{\alpha}_1 = \frac{2 \langle \psi_0 | z | \psi_1 \rangle \langle \psi_1 | V | \psi_1 \rangle \langle \psi_1 | z | \psi_0 \rangle}{[\frac{1}{2} \alpha + \langle \psi_1 | V | \psi_1 \rangle]^2} \\ &= 2 \langle \psi_1 | V | \psi_1 \rangle (1-k)^2. \end{aligned} \quad (29)$$

This implies that

$$\tilde{\alpha}_1 / \tilde{\alpha}_0 = 2 \langle \psi_1 | V | \psi_1 \rangle (1-k) / \alpha = k \quad (30)$$

which is indeed what is found empirically.<sup>3</sup> The additional feature coming from our analysis is the inequality (28), which is indeed verified in the problem as can be seen from the data of Schulman and Musher:  $\alpha_0 = 2.560$ ,  $\alpha_1 = 1.104$ , and  $\alpha = 4.5$ . Hence we obtain  $k = 0.431$ . A test of how good was the approximation (23) is given by checking (28):  $2.560 \leq 4.5 \times 0.569 = 2.5605$ . This indicates that not only was it a good approximation, but also that

$$\psi_{0,1} = 0.569 \psi_1 \quad (31)$$

is quite an accurate representation of  $\psi_0$ . Since

$\psi_{0,1}$  is, *mutatis mutandis*, a good approximation to  $\psi_1$ , the successive orders do nothing but reflect this, since from (12), (23), and (25)

$$\tilde{\psi}_{i,1} \approx (-R_0 V)^i (1-k) \psi_1 \approx k^i (1-k) \psi_1, \quad (32)$$

which leads (approximately) to

$$\sum_{i=0}^{\infty} \tilde{\psi}_{i,1} = \psi_1 \quad (33)$$

in accordance with (14). The fact that (32) is a good approximation is peculiar to this problem, but as we said before (17) does not depend only on that from (9), (30), and (32), it follows that

$$\tilde{\alpha}_i = -k^i (1-k) \tilde{\alpha}_0, \quad k = \tilde{\alpha}_1 / \tilde{\alpha}_0, \quad (34)$$

but it follows also from far less stringent conditions than the validity of (23).

We may summarize the results, so far, in saying that even if  $H_0$  does not have a single contributing excited state, the corresponding reduced resolvent  $R_0$ , in the case of a "H-F hydrogen atom," can be effectively approximated by a one-dimensional inner projection which happens to be the solution of the conventional first-order problem. The result (17) follows from a geometric series fulfilled by the successive orders of the perturbation expansion in this particular case. It follows also from the general considerations of the next section.

### III. VARIATION-PERTURBATION THEORY OF POLARIZABILITIES AND OTHER SECOND-ORDER QUANTITIES

We follow closely a treatment employed previously for dispersion forces<sup>9</sup> given as

$$H = H_0 + V, \quad H_0 \psi_0 = E_0 \psi_0, \quad (35)$$

$$\text{and} \quad \psi_1 = R_0 V \psi_0 \quad (36)$$

with  $R_0$  defined by (13), but with  $H_0$  as an arbitrary zeroth-order operator, we can consider the variational function

$$\tilde{\Psi}(\mu) = \psi_0 + \mu \psi_1 \quad (37)$$

which leads to the functional

$$E[\tilde{\Psi}(\mu)] \equiv \langle \tilde{\Psi}(\mu) | H | \tilde{\Psi}(\mu) \rangle / \langle \tilde{\Psi}(\mu) | \tilde{\Psi}(\mu) \rangle. \quad (38)$$

Using the well-known definitions,

$$\begin{aligned} \epsilon_1 &= \langle \psi_0 | V | \psi_0 \rangle, \quad \epsilon_2 = \langle \psi_0 | V R_0 V | \psi_0 \rangle, \\ \epsilon_3 &= \langle \psi_0 | V R_0 (V - \epsilon_1) R_0 V | \psi_0 \rangle, \end{aligned} \quad (39)$$

$$\Delta = \langle \psi_0 | V R_0^2 V | \psi_0 \rangle.$$

The value of  $\mu$  which makes (38) stationary is<sup>9,10</sup>

$$\bar{\mu} = -\frac{\epsilon_2 - \epsilon_3}{2\Delta\epsilon_2} \left[ 1 - \left( 1 + \frac{4\epsilon_2^2\Delta}{(\epsilon_2 - \epsilon_3)^2} \right)^{1/2} \right] \quad (40)$$

and it leads to

$$\bar{E}[\bar{\Psi}(\bar{\mu})] = E_0 + \epsilon_1 + \epsilon_2 \bar{\mu}. \quad (41)$$

If

$$\epsilon_2^2\Delta/(\epsilon_2 - \epsilon_3)^2 \ll 1, \quad \bar{\mu} \approx (1 - \epsilon_3/\epsilon_2)^{-1}, \quad (42)$$

which is what is embodied in (18)–(20). This general technique can be adapted to the problems under consideration. We first re-examine the “H-F hydrogen atom” of the previous section. We use as the variational function, in connection with  $H(\lambda, \epsilon)$  of (6),

$$\bar{\Psi}(\mu) = \psi_0 + \epsilon\mu\psi_{0,1} \quad (43)$$

where  $\psi_{0,1}$  is given by (12). We get instead of (38)

$$\bar{E}[\mu] = \frac{\langle \bar{\Psi}(\mu) | H_0 + \epsilon z - \lambda V | \bar{\Psi}(\mu) \rangle}{1 + \epsilon^2\mu^2 \langle \psi_{0,1} | \psi_{0,1} \rangle}. \quad (44)$$

From (9), (11), (12), and (39) it follows that

$$\begin{aligned} \epsilon_1 &= 0, & \epsilon_2 &= -\epsilon^2\alpha_0/2, \\ \epsilon_3 &= -\epsilon^2\lambda\alpha_1/2, \\ \Delta &= \langle \psi_{0,1} | \psi_{0,1} \rangle \epsilon^2. \end{aligned} \quad (45)$$

This implies that in this approximation, for  $\lambda = 1$ ,

$$-\frac{\partial^2 \bar{E}[\bar{\mu}]}{\partial \epsilon^2} \Big|_{\epsilon=0} = \alpha_0 \bar{\mu} \quad (46)$$

with  $\bar{\mu}$  given by (40) and (45). In particular, if

$$\langle \psi_{0,1} | \psi_{0,1} \rangle \ll 1,$$

$\bar{\mu}$  is well approximated by

$$\bar{\mu} = (1 - \alpha_1/\alpha_0)^{-1}. \quad (47)$$

We can thus write

$$\alpha \approx \alpha_0 \bar{\mu} \quad (48)$$

with  $\bar{\mu}$  given by (40), and approximate it by

$$\alpha \approx \alpha_0 (1 - \alpha_1/\alpha_0)^{-1} \quad (49)$$

under quite general conditions, subject to verification, which do not require the geometric series as an assumption, and which hold in the example.

It is interesting to notice that if we had used  $T_0 V \varphi_0$  for  $\psi_1$ , i. e., the Brillouin-Wigner resolvent instead of the Schrödinger one, we would have obtained as a counterpart to (41)

$$\bar{E}[\bar{\mu}] = E_0 + \epsilon_1 + \epsilon_2 (1 - \epsilon_3/\epsilon_2)^{-1} \quad (50)$$

expression involving of course Brillouin-Wigner perturbation energies, but with  $\bar{\mu}$  given exactly by (42).<sup>13</sup>

It is clear from (49) that only if  $\alpha_1/\alpha_0 \ll 1$  is it permissible to approximate  $\alpha$  by

$$\alpha \approx \alpha_0 + \alpha_1, \quad (51)$$

i. e., the linear series is in general a bad approximation. Since in the first part of this section we did not specify at all the characteristics of  $H_0$ , the results (48) and (49) are quite general and applicable to a variety of approximation schemes and second-order properties.

In the coupled Hartree-Fock approximation the polarizability<sup>14,15</sup> is determined by the first-order part (in the field) of the self-consistent orbitals – which satisfy H-F equations where the Hamiltonian includes the electromagnetic field. For one-electron systems  $\alpha_{\text{coupled}}$ , as differentiated from the “uncoupled”  $\alpha_0$  of (3), is equal to the exact  $\alpha$ .<sup>3,7</sup> For many-electron systems this is not the case, but  $\alpha_{\text{coupled}}$  often is a good approximation to  $\alpha$ . Schulman and Musher observed that the “geometric” approximation (49) to  $\alpha_{\text{coupled}}$  was surprisingly good.<sup>3</sup> This was a very remarkable result since the effort involved is considerably diminished, but the theoretical grounds for the approximation were absent, and the possibility of extending the applicability to larger atoms and molecules and other electromagnetic properties was tantalizing.

On the basis of the previous discussion we expect Eq. (49) to be a good approximation to the “coupled” H-F polarizability provided that the normalization of the first-order correction to the wave function in the “uncoupled” scheme is small. With appropriate changes the same thing holds for the diamagnetic susceptibilities. The use by Amos and Roberts<sup>4</sup> of the “geometric” approximation, in order to compute ring current contributions to the magnetic susceptibilities of conjugated hydrocarbons, was therefore quite justified. The uncoupled H-F results were origin-dependent. The coupled H-F results are origin-independent, but much more difficult to get. The “geometric” approach introduced by them as a way of computing corrections to the uncoupled results was essentially origin-independent. The condition for this procedure to hold is that  $\psi_0 + \epsilon\bar{\mu}\psi_{0,1}$  is a good approximation to  $\psi$ , the coupled Hartree-Fock result, and that  $\bar{\mu}$  is well given by a formula comparable to (47).

#### IV. CONCLUSIONS

The “geometric” approach in perturbation theory proved to be a remarkable tool to treat second-order properties.<sup>3,4</sup> It was based on the factual ob-

servation that the successive perturbation corrections to the polarizability of the "Hartree-Fock hydrogen atom"<sup>5</sup> do form a geometric series. The final formula was conjectured to be applicable to other systems, and this was verified.<sup>3,4</sup>

We studied the reasons for the peculiar behavior of the hydrogen atom, and even though there are no reasons to believe that the perturbation series is geometric, a variation perturbation approach<sup>9,10</sup> yields a result which contains the geometric approximation.

$$\alpha \approx \alpha_0(1 - \alpha_1/\alpha_0)^{-1}. \quad (52)$$

This formula holds regardless of the fact that  $\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$ , etc., do not form a geometric series, and

is valid for polarizabilities, susceptibilities, and in general for any second-order property within the framework of the Rayleigh-Schrödinger theory. The condition for its validity is that the normalization of the first-order correction  $\Delta$  satisfies  $\Delta \ll 1$ . Otherwise (48) holds with  $\bar{\mu}$  given by (40). The unperturbed  $H_0$  can be arbitrarily chosen. In particular it can be the uncoupled Hartree-Fock operator.

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