Efficient elimination of response parameters in molecular property calculations for variational and nonvariational energies

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A general method is presented for the efficient elimination of response parameters in molecular property calculations for variational and nonvariational energies. For variational energies, Wigner's $2n+1$ rule is obtained as a special case of the more general k_{2n+1} rule, which states that for a subset of k perturbations within a total set of $z \geq k$ perturbations, response parameters may be eliminated according to the $2n+1$ rule (normally applied to the full set of perturbations). Nonvariational energies may be treated by introducing Lagrange multipliers that satisfy the stronger $2n+2$ rule for the k perturbations, while the wave-function parameters still satisfy the $2n+1$ rule for the k perturbations. The corresponding rule for nonvariational energies is referred to as the $k_{2n+1,2n+2}$ rule. For $k=z$, the well-known $2n+2$ rule for the multipliers is reproduced, while the wave-function parameters satisfy the $2n+1$ rule. The application of the k_{2n+1} and $k_{2n+1,2n+2}$ rules minimizes the total number of response equations to be solved when the molecular property contains k extensive perturbations (e.g., geometrical derivatives) and $z-k$ intensive perturbations (e.g., electric fields). [DOI: 10.1063/1.3023123]

I. INTRODUCTION

Molecular properties are essential quantities in quantum-chemical calculations as they represent the link between theory and experiment. For static perturbations, molecular properties may be obtained as energy derivatives with respect to perturbation strengths evaluated at zero perturbation strength. Similarly, for periodic time-dependent perturbations, molecular properties may be obtained as perturbation-strength derivatives of the time-averaged quasienergy.[1,2] In both cases, the time-consuming step in molecular property calculations is the iterative solution of response equations. Thus, to evaluate molecular properties in an efficient manner, the underlying structure of the energy derivatives must be exploited to minimize the number of response equations that need to be solved.

When molecular properties are evaluated, the number of components in the different classes of perturbations may differ significantly. In particular, for certain classes of perturbations, the number of perturbations may be independent of the size of the molecule (e.g., homogeneous electric or magnetic fields). For other classes, their number may be proportional to the size of the molecule (e.g., nuclear displacements or nuclear magnetic moments). We term these perturbations *intensive* and *extensive*, respectively. Except in the smallest molecular systems, the extensive perturbations have many more components than the intensive perturbations. For reasons of efficiency, it is therefore better to reduce the order of the responses equations that must be solved for the extensive perturbations rather than to reduce the total order for all (extensive and intensive) perturbations. For a general set of perturbations $ab\ldots k\ldots z$, where $ab\ldots k$ are extensive and $(k+1)\ldots z$ are intensive, we here discuss how a molecular property represented by the energy derivative with respect to these perturbations $E^{ab\ldots k\ldots z}$ may be evaluated in a way that minimizes the number of response equations to be solved.

For a variational energy, we may in general apply Wigner's $2n+1$ rule,[3] according to which the $(2n+1)$th energy derivative can be evaluated from response parameters up to order n. For the mixed extensive-intensive property $E^{ab\ldots k\ldots z}$, the $2n+1$ rule is then applied to the full set of perturbations $ab\ldots k\ldots z$. In this paper, we derive the more general k_{2n+1} rule, which states that the $2n+1$ rule can be applied separately to the extensive perturbations $ab\ldots k$. As the number of extensive perturbations $ab\ldots k$ is smaller than the total number of perturbations $ab\ldots k\ldots z$, the order to which extensive response parameters must be evaluated is thus further reduced relative to what is required by the usual $2n+1$ rule. This reduction for the extensive perturbations occurs at the expense of having to calculate higher-order response parameters for the intensive perturbations. However, except for the smallest systems, the associated increase in the number of intensive response parameters to be determined is insignificant compared with the reduction in the number of extensive response parameters that need to be solved, leading to an overall reduction in computational effort.

Our discussion extends also to nonvariational energies, which are treated by introducing Lagrange multipliers.[4,5] In

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particular, we show that the k_{2n+1} rule for the response parameters still applies to perturbation-strength derivatives of the Lagrangian, and that the multipliers obey the stronger $2n+2$ rule for the k extensive perturbations, giving the $k_{2n+1,2n+2}$ rule for nonvariational energies. When all perturbations belong to the same class (intensive or extensive) or if all are treated equally, this rule reduces to the standard $2n+2$ rule for the Lagrange multipliers[6] and the $2n+1$ rule for the wave-function parameters.

The k_{2n+1} and $k_{2n+1,2n+2}$ rules are *direct* in the sense that all terms that do not comply with the chosen rule may simply be removed from the energy (or Lagrangian) derivative.

For variational wave functions, it has long been standard practice to use Wigner's $2n+1$ rule to reduce the number of response equations to be solved when calculating molecular properties–see, for example, the monograph by Epstein and references therein.[7] For nonvariational energies such as those of coupled-cluster (CC) theories, a similar reduction is obtained using the Lagrangian technique, applying the $2n+1$ rule to the wave-function parameters and the $2n+2$ rule to the Lagrange multipliers.[6]

The evaluation of geometrical derivatives may be viewed as a property calculation with a perturbation-dependent basis set. In the 1970s and 1980s, much effort was directed toward the efficient calculation of such derivatives, using analytic techniques.[8–10] In view of their general importance in chemistry and the high cost of their evaluation, it becomes essential that these derivatives are evaluated using the minimal number of response equations.

Most importantly, molecular gradients in Hartree–Fock (HF) theory can be calculated directly from the wave function, without solving first-order coupled-perturbed HF (CPHF) equations, as demonstrated by Pulay in 1969.[8] Later, this important result was extended to correlated electronic-structure methods by Handy and Schaefer,[11] who demonstrated how to avoid solving the first-order CPHF equations in the calculation of derivatives from truncated configuration interaction (CI) wave functions, using a turn-over rule. The Handy–Schaefer technique was subsequently applied to second- and third-order Møller–Plesset (MP) theory,[12] to fourth-order MP theory,[13–16] and to CC theory.[17,18] The elimination of the need for solving first-order CPHF equations in analytic gradient calculations may be viewed as a special case of the $1_{2n+1,2n+2}$ rule.

For molecular Hessians of nonvariational methods, the Handy–Schaefer technique was used to avoid the solution of the second-order CPHF equations in CC and MP theories, in the same way as for molecular gradients.[19] We note that in the Lagrangian formulation of energy derivatives and molecular properties, the elimination of response parameters follows the same scheme as for variational energies, thereby making the application of the Handy–Schaefer technique unnecessary, to all orders in the perturbation, as demonstrated for CC molecular gradients and Hessians in Ref. 20.

In the calculation of MP2 second derivatives where one set of perturbations is extensive (nuclear displacements) and the other intensive (electric field components), Simandiras *et al.*[21] showed how the solution of the first-order CPHF equations can be avoided for the extensive perturbations. A similar technique was used by Gauss[22] for evaluating MP2 shielding constants using London orbitals. Using the Lagrangian method, Cybulski and Bishop[23] derived an asymmetric form for the analytic second derivative of a general nonvariational wave function, which may be viewed as a special case of the general $1_{2n+1,2n+2}$ rule discussed here.

Clearly, the k_{2n+1} and $k_{2n+1,2n+2}$ rules are extremely important for evaluating higher-order molecular properties containing mixed extensive and intensive perturbations, allowing the largest possible number of response parameters to be eliminated from the calculations.

The outline of the paper is as follows. In Sec. II, we discuss the evaluation of molecular properties in variational and nonvariational theories. In Sec. III, we derive the general k_{2n+1} rule for a variational energy, and in Sec. IV we extend the formalism to include nonvariational energies using the Lagrangian technique. In Sec. V, we discuss the use of the k_{2n+1} ($k_{2n+1,2n+2}$) rule for a few selected properties. Finally, we give some concluding remarks in Sec. VI.

II. EVALUATION OF MOLECULAR PROPERTIES

We consider a molecular system perturbed by the perturbations a, b, … that depend on a set of perturbation strengths ε_a, ε_b, …, collectively referred to as $\boldsymbol{\varepsilon}$. In general, we may write the energy as a function of $\boldsymbol{\varepsilon}$ and a set of wave-function parameters $\boldsymbol{\lambda}$,

$$E = E(\boldsymbol{\varepsilon}, \boldsymbol{\lambda}). \tag{1}$$

For time-independent perturbations, the energy function $E(\boldsymbol{\varepsilon}, \boldsymbol{\lambda})$ is represented by the energy itself. For time-dependent perturbations, it is instead represented by the time-averaged quasienergy.[1,2]

In variational theory, the energy is stationary with respect to variations in the $\boldsymbol{\lambda}$ parameters at all perturbation strengths,

$$E_{\boldsymbol{\lambda}} = \frac{\partial E(\boldsymbol{\varepsilon}, \boldsymbol{\lambda})}{\partial \boldsymbol{\lambda}} = 0, \quad \text{for all } \boldsymbol{\varepsilon}, \tag{2}$$

which may be used to determine the $\boldsymbol{\lambda}$ parameters. Molecular properties are determined as perturbation-strength derivatives of the energy evaluated for the unperturbed system,

$$E^{ab\ldots z} = \left. \frac{dE}{d\varepsilon_a d\varepsilon_b \ldots d\varepsilon_z} \right|_{\boldsymbol{\varepsilon}=0}, \tag{3}$$

assuming that the wave-function parameters $\boldsymbol{\lambda}^{(0)}$ for the unperturbed system ($\boldsymbol{\varepsilon}=0$) have been determined. Note that $E_{\boldsymbol{\lambda}}$ refers to a wave-function parameter derivative at a general (zero or finite) perturbation strength, whereas $E^{ab\ldots z}$ is a perturbation-strength derivative evaluated at $\boldsymbol{\varepsilon}=0$.

In approximate theories, the wave-function parameters $\boldsymbol{\lambda}$ frequently do not satisfy the stationary condition Eq. (2) but rather some subsidiary relation

$$e(\boldsymbol{\varepsilon}, \boldsymbol{\lambda}) = 0, \quad \text{for all } \boldsymbol{\varepsilon}. \tag{4}$$

This relation may, for example, represent the amplitude equations in CC theory or the canonical conditions in HF and Kohn–Sham self-consistent field theories, where we impose the condition that the molecular orbitals, in addition to being

optimal, diagonalize the Fock/Kohn–Sham matrix. To retain the variational formulation also in such cases, it is convenient to construct a Lagrangian,

$$L(\varepsilon,\lambda,\bar{\lambda}) = E(\varepsilon,\lambda) + \bar{\lambda}e(\varepsilon,\lambda), \tag{5}$$

where $\bar{\lambda}$ is the collection of Lagrange multipliers associated with the constraints.[4,5] The Lagrangian is variational in the multipliers as well as in the original wave-function parameters

$$L_{\bar{\lambda}} = \frac{\partial L}{\partial \bar{\lambda}} = e(\varepsilon,\lambda) = 0, \tag{6}$$

$$L_{\lambda} = \frac{\partial L}{\partial \lambda} = E_{\lambda} + \bar{\lambda}\frac{\partial e}{\partial \lambda} = 0. \tag{7}$$

The variation with respect to $\bar{\lambda}$ in Eq. (6) gives the equation for λ in Eq. (4) and is trivially satisfied, whereas the variation in λ in Eq. (7) yields a set of linear equations that determine the multipliers. From this Lagrangian, molecular properties may be determined as perturbation-strength derivatives evaluated at $\varepsilon=0$, equivalent to the variational case in Eq. (3),

$$E^{ab\ldots z} = L^{ab\ldots z} = \left.\frac{dL}{d\varepsilon_a d\varepsilon_b \ldots d\varepsilon_z}\right|_{\varepsilon=0}. \tag{8}$$

As discussed in the Sec. I, we classify the perturbations as either extensive or intensive and consider here derivatives $E^{ab\ldots k\ldots z}$ that contain k extensive perturbations $ab\ldots k$ followed by $z-k$ intensive perturbations $(k+1)(k+2)\ldots k$. In the following, the symbol k refers either to a particular perturbation in the set $ab\ldots k\ldots z$ or to the position of k in the list $ab\ldots k\ldots z$, depending on the context.

For variational energies, we shall derive the k_{2n+1} rule, which eliminates the largest possible number of response parameters of the extensive perturbations by application of the $2n+1$ rule to the set $ab\ldots k$ exclusively. For nonvariational energies, we use the Lagrangian technique and derive the $k_{2n+1,2n+2}$ rule, which eliminates wave-function parameters according to the $2n+1$ rule and Lagrange multipliers according to the $2n+2$ rule for the set $ab\ldots k$.

III. THE k_{2n+1} RULE FOR VARIATIONAL ENERGIES

In this section, we consider variational energies, which satisfy the stationary condition in Eq. (2). First, in Sec. III A, we discuss the form of the response equations, from which the wave-function response parameters may be determined. In Sec. III B, we see how the stationary condition enables us to eliminate response parameters from perturbation-strength derivatives of the energy in a systematic manner, leading to the k_{2n+1} rule discussed in Sec. III C.

A. Response equations

The λ parameters may be expanded in terms of the perturbation strength parameters,

$$\lambda = \lambda^{(0)} + \lambda^{(1)} + \lambda^{(2)} + \cdots, \tag{9}$$

where $\lambda^{(0)}$ are the optimized parameters for the unperturbed system $(\varepsilon=0)$ and

$$\lambda^{(1)} = \sum_a \varepsilon_a \lambda^a, \quad \lambda^a = \left.\frac{\partial \lambda}{\partial \varepsilon_a}\right|_{\varepsilon=0}, \tag{10}$$

$$\lambda^{(2)} = \frac{1}{2}\sum_{ab} \varepsilon_a \varepsilon_b \lambda^{ab}, \quad \lambda^{ab} = \left.\frac{\partial^2 \lambda}{\partial \varepsilon_a \partial \varepsilon_b}\right|_{\varepsilon=0}, \tag{11}$$

and so on, where the summations are over all perturbations and the response parameters are symmetric with respect to index permutations $\lambda^{ab}=\lambda^{ba}$.

To determine a given response parameter $\lambda^{ab\ldots p}$, where p is an arbitrary index in the $ab\ldots z$ list, we differentiate the stationary condition in Eq. (2) with respect to the corresponding perturbation strengths and evaluate at $\varepsilon=0$,

$$E_{\lambda}^{ab\ldots p} = \left.\frac{d^p E_{\lambda}}{d\varepsilon_a d\varepsilon_b \cdots d\varepsilon_p}\right|_{\varepsilon=0} = 0. \tag{12}$$

In the short-hand notation,

$$E^{N,0} = \left.\frac{\partial^N E}{\partial \lambda^N}\right|_{\varepsilon=0}, \tag{13}$$

$$E^{N,ab\ldots p} = \left.\frac{\partial^{N+p} E}{\partial \lambda^N \partial \varepsilon_a \partial \varepsilon_b \cdots \partial \varepsilon_p}\right|_{\varepsilon=0}, \tag{14}$$

we may then write the stationary conditions (response equations) up to second order as

$$E^{1,0} = 0, \tag{15}$$

$$E^{2,0}\lambda^a + E^{1,a} = 0, \tag{16}$$

$$E^{2,0}\lambda^{ab} + E^{2,a}\lambda^b + E^{2,b}\lambda^a + E^{3,0}\lambda^a\lambda^b + E^{1,ab} = 0. \tag{17}$$

We note that the highest-order response parameter $\lambda^{ab\ldots p}$ always enters as $E^{2,0}\lambda^{ab\ldots p}$ in the pth-order response equation

$$E^{2,0}\lambda^{ab\ldots p} + M_{p-1} = 0, \tag{18}$$

where M_{p-1} contains only response parameters of order $p-1$ and lower. We may thus write the response parameters in the form

$$\lambda^{ab\ldots p} = -(E^{2,0})^{-1} M_{p-1}. \tag{19}$$

Hence, by solving for the λ^a, λ^{ab}, …, $\lambda^{ab\ldots p}$ parameters successively, substituting the lower-order parameters already solved for into the higher-order equations, we may generate the full set of response parameters.

B. Parameter elimination

Before discussing general energy derivatives, let us consider as a special case the second-order energy derivative

$$E^{ab} = E^{0,ab} + E^{1,b}\lambda^a + (E^{2,0}\lambda^a + E^{1,a})\lambda^b + E^{1,0}\lambda^{ab}. \tag{20}$$

From this expression, we may eliminate λ^{ab} since it multiplies the zero-order stationary condition in Eq. (15) and λ^b since it multiplies the first-order stationary condition in Eq.

TABLE I. Elimination of the pth-order response parameter $\lambda^{ab\cdots p}$ in the total energy derivative $E^{ab\cdots z}$ affects the parameters multiplying $\lambda^{ab\cdots p}$. The affected parameters, which range from order one to order $z-p$, may then no longer be eliminated.

Eliminated parameter	Affected parameters	Order
$\lambda^{ab\cdots p}$	$\lambda^{(p+1)},\ldots,\lambda^{z}$	1
	$\lambda^{(p+1)(p+2)},\ldots,\lambda^{(z-1)z}$	2
	$\vdots$	$\vdots$
	$\lambda^{(p+1)(p+2)\cdots z}$	$z-p$

(16). The second-order energy may therefore be written in the simplified form

$$E^{ab} = E^{0,ab} + E^{1,b}\lambda^{a}. \tag{21}$$

Note that λ^a cannot be eliminated from this expression since, following the elimination of λ^b by the removal of $(E^{2,0}\lambda^a + E^{1,a})\lambda^b$ from the second-order energy derivative, we also removed $E^{2,0}\lambda^a\lambda^b$ so that λ^a no longer multiplies a stationary condition $(E^{2,0}\lambda^b + E^{1,b})\lambda^a$. Alternatively, we could have eliminated λ^a while retaining λ^b in Eq. (20).

Our discussion of the second-order energy illustrates how we may eliminate certain response parameters from the energy derivatives but not all independently. Let us now consider this elimination for a general derivative $E^{ab\cdots p\cdots z}$, where p is an arbitrary index. Differentiating the energy with respect to the first p perturbations, we note that the pth-order energy derivative takes the form

$$\frac{dE}{d\varepsilon_a d\varepsilon_b \cdots d\varepsilon_p} = E_{\lambda}\frac{\partial^p \lambda}{\partial\varepsilon_a\,\partial\,\varepsilon_b \cdots \partial\varepsilon_p} + \text{terms independent of } \frac{\partial^p \lambda}{\partial\varepsilon_a\,\partial\,\varepsilon_b \cdots \partial\varepsilon_p}, \tag{22}$$

where the highest-order λ derivative $\partial^p\lambda/\partial\varepsilon_a\partial\varepsilon_b\cdots\partial\varepsilon_p$ occurs only once, multiplied by $E_\lambda=0$, just like λ^{ab} occurs only once in Eq. (20). Further differentiation and evaluation at $\varepsilon=0$ now yields

$$E^{ab\cdots p\cdots z} = E_{\lambda}^{(p+1)\cdots z}\lambda^{ab\cdots p} + \text{terms independent of } \lambda^{ab\cdots p}, \tag{23}$$

where $\lambda^{ab\cdots p}$ still only occurs once, assuming that all perturbations are different. (If two or more perturbations are identical, they can be treated as symmetry-related but different perturbations.) Next, differentiating Eq. (23) with respect to $\lambda^{ab\cdots p}$ and invoking the stationary condition in Eq. (12), $E_{\lambda}^{(p+1)\cdots z}=0$, we conclude that $E^{ab\cdots z}$ is stationary with respect to $\lambda^{ab\cdots p}$. Since p was chosen arbitrarily, $E^{ab\cdots z}$ must be stationary with respect to all possible responses,

$$\frac{\partial E^{ab\cdots z}}{\partial \lambda^{ab\cdots p}} = 0, \quad p = a,b,\ldots,z. \tag{24}$$

Consequently, we may eliminate any $\lambda^{ab\cdots p}$ except $\lambda^{(0)}$ from $E^{ab\cdots z}$ but, in doing so, we modify the contributions from all parameters involving $(p+1),\ldots,z$ as depicted in Table I and are no longer free to eliminate these parameters.

TABLE II. Systematic elimination of parameters containing the $ab\ldots k$ perturbations for the calculation of $E^{ab\ldots k|(k+1)\ldots z}$.

Eliminated parameters	Affected parameters
$\lambda_{k|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{0|*}^{ab\ldots k|(k+1)\ldots z}$
$\lambda_{k-1|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{1_\downarrow|*}^{ab\ldots k|(k+1)\ldots z}$
$\lambda_{k-2|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{2_\downarrow|*}^{ab\ldots k|(k+1)\ldots z}$
$\vdots$	$\vdots$
$\lambda_{k-v|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{v_\downarrow|*}^{ab\ldots k|(k+1)\ldots z}$

Consider, for example, how $\lambda^{(p+1)}$ occurs in $E^{ab\cdots z}$ before the elimination of any λ terms,

$$E^{ab\ldots z} = E_{\lambda}^{a\ldots p(p+2)\ldots z}\lambda^{(p+1)} + \text{terms independent of } \lambda^{(p+1)}. \tag{25}$$

Since $\lambda^{(p+1)}$ multiplies a response equation of order $z-1$, it may be eliminated. However, if we first eliminate $\lambda^{ab\cdots p}$ using Eq. (23), then we have also removed certain terms from the factor in front of $\lambda^{(p+1)}$ in Eq. (25) since $\lambda^{ab\cdots p}$ is contained in $E_{\lambda}^{a\ldots p(p+2)\ldots z}$. Thus, after the elimination of $\lambda^{ab\cdots p}$, $\lambda^{(p+1)}$ no longer multiplies a vanishing response equation and cannot be eliminated. However, after elimination of $\lambda^{ab\cdots p}$, we are still free to eliminate parameters unaffected by the elimination procedure in Table I—that is, all parameters involving one or more of the $ab\ldots p$ perturbations such as λ^a or $\lambda^{ab\ldots p(p+2)\ldots z}$. In short, we may eliminate any response parameter $\lambda^{ab\cdots p}$ from $E^{ab\cdots z}$ but this precludes the further elimination of all response parameters entering the factor multiplying $\lambda^{ab\cdots p}$.

C. The k_{2n+1} rule

To keep track of the parameters, we introduce the notation $\lambda_{r|s}^{ab\ldots k|(k+1)\ldots z}$ to denote the set of λ parameters of orders r in the $ab\ldots k$ indices and s in the $(k+1)\ldots z$ indices. In addition, an asterisk indicates that all orders are included in a given set, whereas $r_\downarrow$ indicates that only orders r and lower are included. For example, $\lambda_{2_\downarrow|*}^{abcd|ef}$ is the set of λ parameters up to second order in $abcd$ and of all orders in ef.

We are now in position to eliminate the largest possible number of response parameters referencing the extensive $ab\ldots k$ perturbations by use of Table I. First, by eliminating $\lambda_{k|*}^{ab\ldots k|(k+1)\ldots z}$, we affect parameters in the set $\lambda_{0|*}^{ab\ldots k|(k+1)\ldots z}$. Similarly, elimination of $\lambda_{k-1|*}^{ab\ldots k|(k+1)\ldots z}$ affects the $\lambda_{1_\downarrow|*}^{ab\ldots k|(k+1)\ldots z}$ parameters. This scheme is depicted in Table II. The elimination may be continued until the eliminated and affected parameters overlap. From the last line in Table II, we see that we may eliminate parameters if $k-v>v$—that is, when

$$v < \frac{k}{2}. \tag{26}$$

Equation (26) may be viewed as a $2n+1$ rule within the $ab\ldots k$ indices and will be referred to as the k_{2n+1} *rule for a variational energy*. When evaluating $E^{ab\ldots k\ldots z}$, we may eliminate all λ parameters of order greater than $n=\lfloor k/2\rfloor$ in the $ab\ldots k$ indices, where $\lfloor k/2\rfloor$ is the largest integer less than

TABLE III. Elimination of parameters involving either a or b in the $E^{ab|cde}$ derivative. Elimination of the parameters in bold font minimizes the number of response equations to be solved. For simplicity, we have not included any $\downarrow$ in the table. If a given parameter is eliminated, $\downarrow$ should be added to the affected parameter, for example, elimination of $\lambda_{1|2}^{a|cde}$ affects $\lambda_{1_\downarrow|1_\downarrow}^{b|cde}$, whereas the elimination of $\lambda_{1|1}^{b|cde}$ affects $\lambda_{1_\downarrow|2_\downarrow}^{a|cde}$.

Eliminated/affected a parameter	Eliminated/affected b parameter
$\boldsymbol{\lambda}_{1\|3}^{a\|cde}$	$\lambda_{1\|0}^{b\|cde}$
$\boldsymbol{\lambda}_{1\|2}^{a\|cde}$	$\lambda_{1\|1}^{b\|cde}$
$\lambda_{1\|1}^{a\|cde}$	$\boldsymbol{\lambda}_{1\|2}^{b\|cde}$
$\lambda_{1\|0}^{a\|cde}$	$\boldsymbol{\lambda}_{1\|3}^{b\|cde}$

or equal to $k/2$. In other words, wave-function parameters to order n in the $ab\ldots k$ indices determine energy derivatives to order $2n+1$ within these indices. We use the notation $E^{ab\ldots k|(k+1)\ldots z}$ to indicate that the energy derivative is evaluated according to the k_{2n+1} rule.

If k is even, certain eliminations may be performed in addition to the k_{2n+1} rule because the even-order $\lambda_{k/2|*}^{ab\ldots k|(k+1)\ldots z}$ parameters have not been touched. We may therefore eliminate half of the terms of order $k/2$ in the $ab\ldots k$ perturbations, for example, either the set $\lambda_{k/2|*}^{ab\ldots k/2|(k+1)\ldots z}$ or the set $\lambda_{k/2|*}^{(k/2+1)\ldots k|(k+1)\ldots z}$. Similarly, the remaining parameters of order $k/2$ in $ab\ldots k$ enter in pairs and half of them may be eliminated. However, this may not be the best way of eliminating terms of order $k/2$ in the $ab\ldots k$ indices, as illustrated for $k=2$ in Sec. III C 1 below.

By treating all perturbations on an equal footing and letting $k=z$, we eliminate parameters of order greater than $\lfloor z/2 \rfloor$ in all perturbations. This is the standard $2n+1$ rule, which states that for a variational energy, the energy derivative to order $2n+1$ is determined by response parameters to order n.

The 1_{2n+1} rule discussed in the introduction is obtained by letting $k=a$. We may then eliminate all parameters of order greater than $\lfloor 1/2 \rfloor=0$ in the a index—that is, we only need to include $\lambda_{0|*}^{a|bc\ldots z}$ in the evaluation of the energy and all parameters involving a are thus eliminated.

1. Special case: 2_{2n+1} rule

As described above, when k is even, we may eliminate all response parameters of order greater than $\lfloor k/2 \rfloor=k/2$ in the $ab\ldots k$ indices. In addition, half of the parameters of order $k/2$ in the $ab\ldots k$ indices may be eliminated. This may be done in several ways.

Consider the case where we have two extensive perturbations a and b $(k=2)$ and three intensive perturbations cde. When evaluating E^{abcde}, we may immediately eliminate all terms quadratic in ab in accordance with the 2_{2n+1} rule—that is, the set $\lambda_{2|*}^{ab|cde}$ is eliminated. In addition, we may eliminate some parameters containing either a or b, for example, elimination of $\lambda_{1|2}^{a|cde}$ affects $\lambda_{1_\downarrow|1_\downarrow}^{b|cde}$. This elimination scheme is depicted in Table III.

One possible elimination scheme is the elimination of all parameters containing a, $\lambda_{1|*}^{a|cde}$ (the left column of Table III), thereby eliminating the a perturbation completely. This reproduces the 1_{2n+1} rule. However, to minimize the number of response equations to be solved, it is advantageous to eliminate parameters containing the intensive cde perturbations to higher order—that is, we may eliminate all parameters containing a or b coupled to cde to second and third order. These parameters are shown in bold font in Table III.

In general, when evaluating $E^{ab\ldots k\ldots z}$ for even k, we first eliminate all parameters of orders greater than $k/2$ in the extensive perturbations $ab\ldots k$. Subsequently, we may eliminate half of the parameters of order $k/2$ in the $ab\ldots k$ indices. The eliminated parameters may be chosen so as to minimize the orders of the intensive perturbations $(k+1)\ldots z$ as exemplified above. In fact, the elimination scheme described above corresponds to applying the $2n+1$ rule within the $(k+1)\ldots z$ perturbations for response parameters of order $k/2$ in the $ab\ldots k$ perturbations. This procedure is of course secondary to that in Table II, where parameters coupling the extensive perturbations $ab\ldots k$ are eliminated.

In the next section, we extend the formalism to nonvariational energies. We shall see that the k_{2n+1} rule is also applicable to a Lagrangian function and that the Lagrange multipliers obey the somewhat stronger $2n+2$ rule within the $ab\ldots k$ perturbations.

IV. MOLECULAR PROPERTIES FOR A NONVARIATIONAL ENERGY

We here consider a nonvariational energy function, where the wave-function parameters are determined from an equation of the form in Eq. (4). Molecular properties are determined as perturbation-strength derivatives of the Lagrangian $L(\varepsilon,\lambda,\bar{\lambda})$ in Eq. (5), evaluated at zero perturbation strengths as in Eq. (8). The wave-function parameters λ and the Lagrange multipliers $\bar{\lambda}$ are determined from Eqs. (6) and (7) such that the Lagrangian is variational in both λ and $\bar{\lambda}$.

A. Response equations

The $\bar{\lambda}$ parameters are expanded in orders of the perturbation in the same way as was done for the λ parameters in Sec. III A,

$$\bar{\lambda} = \bar{\lambda}^{(0)} + \bar{\lambda}^{(1)} + \bar{\lambda}^{(2)} + \ldots, \tag{27}$$

where

$$\bar{\lambda}^{(1)} = \sum_a \varepsilon_a \bar{\lambda}^a, \quad \bar{\lambda}^a = \left.\frac{\partial \bar{\lambda}}{\partial \varepsilon_a}\right|_{\varepsilon=0}, \tag{28}$$

$$\bar{\lambda}^{(2)} = \frac{1}{2}\sum_{ab} \varepsilon_a \varepsilon_b \bar{\lambda}^{ab}, \quad \bar{\lambda}^{ab} = \left.\frac{\partial^2 \bar{\lambda}}{\partial \varepsilon_a \partial \varepsilon_b}\right|_{\varepsilon=0}, \tag{29}$$

such that $\bar{\lambda}^{(0)}$, $\bar{\lambda}^a$, $\bar{\lambda}^{ab}$, … become the multiplier parameters. In analogy with Eq. (12), the λ and $\bar{\lambda}$ parameters to different orders such as $\lambda^{ab\ldots p}$ and $\bar{\lambda}^{ab\ldots p}$ may be determined from the differentiated variational equations [Eqs. (6) and (7)],

$$L_{\bar{\lambda}}^{ab\ldots p} = \left.\frac{d^p L_{\bar{\lambda}}}{d\varepsilon_a d\varepsilon_b \ldots d\varepsilon_p}\right|_{\varepsilon=0} = 0, \tag{30}$$

$$L_{\lambda}^{ab\ldots p} = \left. \frac{d^p L_{\lambda}}{d\varepsilon_a d\varepsilon_b \ldots d\varepsilon_p} \right|_{\varepsilon=0} = 0. \tag{31}$$

The procedure for solving for a general $\lambda^{ab\ldots p}$ parameter is to solve Eqs. (30) and (31) for lower-order λ and $\bar{\lambda}$ parameters and substitute these into the higher-order response equations until $\lambda^{ab\ldots p}$ has been determined. In each step, the λ parameter is found from Eq. (30) and then substituted into Eq. (31) to solve for the corresponding multiplier.

B. The Lagrangian $k_{2n+1,2n+2}$ rule

By differentiating the Lagrangian in Eq. (5) with respect to the ε_a, ε_b, …, ε_p perturbation strengths, we see that the pth-order Lagrangian derivative always has the structure

$$\frac{dL}{d\varepsilon_a d\varepsilon_b \ldots d\varepsilon_p} = L_{\bar{\lambda}} \frac{\partial^p \bar{\lambda}}{\partial \varepsilon_a \partial \varepsilon_b \ldots \partial \varepsilon_p} + L_{\lambda} \frac{\partial^p \lambda}{\partial \varepsilon_a \partial \varepsilon_b \ldots \partial \varepsilon_p} + \text{terms independent of } \frac{\partial^p \bar{\lambda}}{\partial \varepsilon_a \partial \varepsilon_b \ldots \partial \varepsilon_p} \text{ and } \frac{\partial^p \lambda}{\partial \varepsilon_a \partial \varepsilon_b \ldots \partial \varepsilon_p}. \tag{32}$$

Hence, $\bar{\lambda}^{ab\ldots p}$ and $\lambda^{ab\ldots p}$ enter the zth-order Lagrangian derivative at $\varepsilon=0$, $L^{ab\ldots z}$, as

$$L^{ab\ldots z} = L_{\bar{\lambda}}^{(p+1)\ldots z} \bar{\lambda}^{ab\ldots p} + L_{\lambda}^{(p+1)\ldots z} \lambda^{ab\ldots p} + \text{terms independent of } \bar{\lambda}^{ab\ldots p} \text{ and } \lambda^{ab\ldots p}. \tag{33}$$

So $\bar{\lambda}^{ab\ldots p}$ and $\lambda^{ab\ldots p}$ simply multiply the response equations in Eqs. (30) and (31) to order $z-p$. The Lagrangian derivative $L^{ab\ldots z}$ is therefore variational in all λ parameters and multipliers, analogously to the variational energy derivative in Eq. (24),

$$\frac{\partial L^{ab\ldots z}}{\partial \lambda^{ab\ldots p}} = \frac{\partial L^{ab\ldots z}}{\partial \bar{\lambda}^{ab\ldots p}} = 0; \quad p = a,b,\ldots z. \tag{34}$$

Any multiplier or wave-function parameter to order p may therefore be eliminated, thereby affecting parameters to order $z-p$, which then may no longer be eliminated. More precisely, elimination of $\bar{\lambda}^{ab\ldots p}$ affects the λ parameters involving the $(p+1)\ldots z$ indices but does not affect any $\bar{\lambda}$ parameters as these occur linearly in the Lagrangian in Eq. (5). Elimination of $\lambda^{ab\ldots p}$ affects both $\bar{\lambda}$ and λ parameters involving the $(p+1)\ldots z$ indices as both $\bar{\lambda}$ and λ enter in L_{λ}, see Eq. (7). We also note that zeroth-order λ parameters $\lambda^{(0)}$ may not be eliminated since they enter in all terms.

We now consider the case where we want to calculate the zth-order derivative $L^{ab\ldots k\ldots z}$ and where we want to eliminate as many parameters (both λ and $\bar{\lambda}$) as possible referring to the $ab\ldots k$ perturbations. The elimination procedure, which follows the one used in Sec. III C, is depicted in Tables IV and V for the λ and $\bar{\lambda}$ parameters, respectively.

From Table IV, it follows that elimination of the set of parameters $\lambda_{k-v|*}^{ab\ldots k|(k+1)\ldots z}$ affects both the λ set $\lambda_{v_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$ and the $\bar{\lambda}$ set $\bar{\lambda}_{v_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$. We may therefore continue the elimination procedure depicted in Table IV until the eliminated and the affected λ parameters overlap—that is, we must have

$$v < \frac{k}{2}. \tag{35}$$

We thus see that the k_{2n+1} rule described in Sec. III C is still valid for the λ parameters in the Lagrangian formulation. When k is even, however, we do not eliminate any λ parameters of order $k/2$ in the $ab\ldots k$ indices as was done in Sec. III C 1. Instead, we use this freedom to impose a stronger rule on the multipliers.

By eliminating the λ parameters to order higher than $\lfloor k/2 \rfloor$ in the $ab\ldots k$ indices in Table IV, we affect λ parameters and multipliers up to order $(k-1)/2$ for uneven k and $(k/2)-1$ for even k. Therefore, these multipliers cannot be eliminated but higher-order multipliers may still be eliminated as long as they only affect λ parameters of order $\lfloor k/2 \rfloor$ and below in the $ab\ldots k$ indices. (Recall that for even k we have not manipulated any λ parameters of order $k/2$ in the $ab\ldots k$ indices.) Using the notation in Table V, we see that we may eliminate the set of multipliers $\bar{\lambda}_{k-w|*}^{ab\ldots k|(k+1)\ldots z}$, thereby affecting the set of λ parameters $\lambda_{w_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$ as long as

$$w \leq \lfloor k/2 \rfloor. \tag{36}$$

Therefore, for even k, we may eliminate the set $\bar{\lambda}_{(k/2)|*}^{ab\ldots k|(k+1)\ldots z}$ and all higher-order multipliers in the $ab\ldots k$ indices. We have thus obtained a $2n+2$ rule for the multipliers within the $ab\ldots k$ indices. We only need multipliers to order n in the $ab\ldots k$ indices to determine the Lagrangian derivative to order $2n+2$ within these indices. In particular, if $k=z$, all perturbations are treated on an equal footing and we obtain the well-known $2n+2$ rule,[6] which states that $(2n+2)$th-order Lagrangian derivatives are determined from nth-order multipliers.

In summary, we have derived the $k_{2n+1,2n+2}$ *rule for a*

TABLE IV. Systematic elimination of λ parameters containing the $ab\ldots k$ perturbations for the calculation of $L^{ab\ldots k|(k+1)\ldots z}$.

Eliminated parameter	Affected λ parameters	Affected $\bar{\lambda}$ parameters
$\lambda_{k|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{0|*}^{ab\ldots k|(k+1)\ldots z}$	$\bar{\lambda}_{0|*}^{ab\ldots k|(k+1)\ldots z}$
$\lambda_{k-1|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{1_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$	$\bar{\lambda}_{1_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$
⋮	⋮	⋮
$\lambda_{k-v|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{v_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$	$\bar{\lambda}_{v_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$

TABLE V. Systematic elimination of $\bar{\lambda}$ parameters containing the $ab\ldots k$ perturbations for the calculation of $L^{ab\ldots k|(k+1)\ldots z}$.

Eliminated parameter	Affected λ parameters	Affected $\bar{\lambda}$ parameters
$\bar{\lambda}_{k|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{0|*}^{ab\ldots k|(k+1)\ldots z}$	.
$\bar{\lambda}_{k-1|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{1_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$	.
⋮	⋮	⋮
$\bar{\lambda}_{k-w|*}^{ab\ldots k|(k+1)\ldots z}$	$\lambda_{w_{\downarrow}|*}^{ab\ldots k|(k+1)\ldots z}$	.

nonvariational energy in the Lagrangian formulation. When evaluating $L^{ab\ldots k\ldots z}$, λ and $\bar{\lambda}$ parameters may be eliminated in accordance with the $2n+1$ and $2n+2$ rules within the $ab\ldots k$ indices. We refer to the Lagrangian evaluated in accordance with the $k_{2n+1,2n+2}$ rule as $L^{ab\ldots k|(k+1)\ldots z}$, in analogy with the notation of variational theory.

V. EXAMPLES

We have now derived the k_{2n+1} and $k_{2n+1,2n+2}$ rules, which minimize the number of response parameters to be determined for evaluating the energy derivative $E^{ab\ldots k\ldots z}$ when $ab\ldots k$ are extensive perturbations and $(k+1)\ldots z$ are intensive perturbations.

The rules may be applied, for example, to a molecular property containing one extensive (e) and two intensive (i) perturbations E^{eii}, as is the case for the polarizability gradient, which determines the line intensities in Raman spectra, e representing nuclear displacements and i electric field components. In this case, the 1_{2n+1} ($1_{2n+1,2n+2}$) rule tells us that no extensive response parameters (and multipliers) need to be determined to obtain E^{eii}.

For the calculation of the zero-point vibrational (ZPV) contribution to a molecular property, the second derivatives of the molecular property with respect to nuclear coordinates are needed.[24] For example, to calculate the ZPV contribution to the polarizability, we need a fourth-order energy derivative E^{eeii}, with e being nuclear coordinates and i being electric-field components. The number of response equations to be solved is in this case minimized by application of the 2_{2n+1} ($2_{2n+1,2n+2}$) rule. Next, to calculate the ZPV contribution to nuclear magnetic shielding polarizabilities,[25] E^{eeeii} derivatives are needed, with eee being two nuclear coordinates and one nuclear magnetic moment, whereas ii are one electric and one magnetic field component. In that case, the 3_{2n+1} ($3_{2n+1,2n+2}$) rule is the method of choice.

If all perturbations are either extensive or intensive ($k=z$) as for the first hyperpolarizability E^{iii} (i being electric field components), then the z_{2n+1} ($z_{2n+1,2n+2}$) rule reduces to the standard $2n+1$ (and $2n+2$) rule(s).

To illustrate in detail the advantages of the k_{2n+1} rule over the standard $2n+1$ rule, let us consider E^{eeeii} for a variational energy. Straightforward use of the $2n+1$ rule allows us to eliminate all response parameters above second order, retaining the response parameters λ^e, λ^i, λ^{ee}, λ^{ei}, and λ^{ii}. Because the λ^{ee} response has not been eliminated, the number of response equations that need to be solved increases quadratically with system size. On the other hand, if instead we apply the 3_{2n+1} rule, we need the extensive response parameters to first order and the intensive parameters of all orders—that is, λ^e, λ^i, λ^{ei}, λ^{ii}, and λ^{eii}. In this case, we have eliminated the λ^{ee} responses and the number of response equations to be solved increases now only linearly with system size. Clearly, for the evaluation of E^{eeeii}, the 3_{2n+1} rule greatly reduces the total number of response equations to be solved compared with the standard $2n+1$ rule.

VI. CONCLUSION

We have derived the k_{2n+1} rule for variational energies, stating that when calculating the energy derivative $E^{ab\ldots k|(k+1)\ldots z}$, the $2n+1$ rule for the elimination of response parameters may be applied separately to the subset $ab\ldots k$ of perturbations. Typically, this subset comprises all extensive perturbations (whose number increases linearly with system size), in contrast to the remaining intensive perturbations (whose number does not depend on the system size). For nonvariational energies in the Lagrangian formulation, the $k_{2n+1,2n+2}$ rule applies, stating that for the extensive perturbations $ab\ldots k$, the $L^{ab\ldots k|(k+1)\ldots z}$ derivative complies with the $2n+1$ rule for the wave-function parameters and the $2n+2$ rule for the multipliers. The k_{2n+1} and $k_{2n+1,2n+2}$ rules give the minimum number of response equations to be solved for a molecular property containing k extensive perturbations and $k-z$ intensive perturbations.

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[1] K. Sasagane, F. Aiga, and R. Itoh, J. Chem. Phys. **99**, 3738 (1993).
[2] O. Christiansen, P. Jørgensen, and C. Hättig, Int. J. Quantum Chem. **68**, 1 (1998).
[3] E. Wigner, Math. u. Naturw. Anz. Ung. Akad. Wiss. **53**, 477 (1935).
[4] P. Jørgensen and T. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
[5] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[6] T. Helgaker and P. Jørgensen, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum, New York, 1992).
[7] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).
[8] P. Pulay, Mol. Phys. **17**, 197 (1969).
[9] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem., Symp. **10**, 1 (1976).
[10] *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986).
[11] N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).
[12] E. A. Salter, G. W. Trucks, G. Fitzgerald, and R. J. Bartlett, Chem. Phys. Lett. **141**, 61 (1987).
[13] G. W. Trucks, E. A. Salter, C. Sosa, and R. J. Bartlett, Chem. Phys. Lett. **147**, 359 (1988).
[14] G. W. Trucks, E. A. Salter, J. Noga, and R. J. Bartlett, Chem. Phys. Lett. **150**, 37 (1988).
[15] G. W. Trucks, J. D. Watts, E. A. Salter, and R. J. Bartlett, Chem. Phys. Lett. **153**, 490 (1988).
[16] E. Kraka, J. Gauss, and D. Cremer, J. Mol. Struct. THEOCHEM **234**, 95 (1991).
[17] J. Gauss and D. Cremer, Adv. Quantum Chem. **23**, 205 (1992).
[18] E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989).
[19] E. A. Salter and R. J. Bartlett, J. Chem. Phys. **90**, 1767 (1989).
[20] H. Koch and H. J. Aa. Jensen, P. Jørgensen, T. Helgaker, G. E. Scuseria, and H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990).
[21] E. D. Simandiras, R. D. Amos, and N. C. Handy, Chem. Phys. **114**, 9 (1987).
[22] J. Gauss, Chem. Phys. Lett. **191**, 614 (1992).
[23] S. M. Cybulski and D. M. Bishop, Int. J. Quantum Chem. **49**, 371 (1994).
[24] K. Ruud, P.-O. Åstrand, and P. R. Taylor, J. Chem. Phys. **112**, 2668 (2000).
[25] S. Coriani, A. Rizzo, K. Ruud, and T. Helgaker, Chem. Phys. **216**, 53 (1997).