Editor's Suggestion

Molecular multipoles and (hyper) polarizabilities from the Buckingham expansion: revisited

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Abstract
The Buckingham expansion is important for understanding molecular multipoles and (hyper)polarizabilities. In this study, we give a complete derivation of the Buckingham expansion in the traced form using successive Taylor series. Based on the derivation results, a general Buckingham expansion in the traced form is proposed, from which highly accurate numerical calculations using the finite field method can be achieved. The transformations from the traced multipoles and multipole–multipole polarizabilities to the corresponding traceless counterparts are realized with an auxiliary traced electric field gradient. The applications of the finite field method in this study show good agreements with previous theoretical calculations and experimental measurements.

Keywords: Buckingham expansion, multipole, (hyper)polarizability, finite field method, ab initio calculations

1. Introduction
Multipoles and (hyper)polarizabilities are important molecular interactions [1, 2]. The interactions between molecules and external electric fields and field gradients can be expanded with multipoles in external electric fields and field gradients, which is the well-known multipole expansion. Furthermore, if the molecule is polarizable, the multipoles are also inducible by the field and field gradients. The resultant interactions are expanded to include all the permanent and induced multipoles, with the induced components manifested in the (hyper)polarizabilities, and we denote in this study the resultant expression as the Buckingham expansion [3–5]. Thus, as multiple external electric fields and field gradients $E$ are applied to the polarizable charge distribution $\rho(r)$, which can be expanded by permanent and induced multipoles $M(r)$, the responses via the Buckingham expansion are as shown schematically in figure 1.

The Buckingham expansion is not only of interest theoretically, but also leads to important applications in determining molecular (hyper)polarizabilities [6] and quadrupoles [3, 7]. By designing a four-wire electric field gradient condenser, which induces birefringence (Kerr effects) on the polar molecular system, inherently originated from the anisotropic molecular multipoles/(hyper)polarizabilities as represented by the Buckingham expansion, Buckingham derived the method to detect the molecular quadrupole [3]. This theoretical derivation was realized experimentally with direct detection of the quadrupole of carbon dioxide [7].

Since it is generally difficult to detect molecular hyperpolarizabilities experimentally, except in some small molecules of high symmetry, it is common nowadays to calculate molecular multipoles and (hyper)polarizabilities numerically against high-level ab initio calculations, either using test charges to generate the desired finite external electric field and field gradients [8, 9], or manipulating the electric field tensors directly [10, 11]. Either way, the molecular multipoles and (hyper)polarizabilities can be obtained by finite difference with high accuracy up to $O(E^3)$, in which $E$ denotes the external fields or field gradients. In order to
get numerical multipoles and (hyper)polarizabilities, especially for the multipole–multipole polarizabilities, accurately up to high-order \( n \), the complete Buckingham expansion needs to be known.

To the best of our knowledge, the Buckingham expansion was originally proposed up to the fourth order of electric fields or field gradients in the traceless form, in which all the multipoles and (hyper)polarizabilities are traceless [3, 4]. For \textit{ab initio} calculations, it is more convenient to work instead with traced multipoles and (hyper)polarizabilities. Thus, a general Buckingham expansion in the traced form up to arbitrary order of electric fields or field gradients, as well as the corresponding transformation from traced to traceless multipoles and (hyper)polarizabilities, are desired. Aiming to fill in the gaps, McLean and Yoshimine [12, Applequist [13], and Pedersen et al [11] all derived the transformation from traced to traceless multipoles and (hyper)polarizabilities, in which the transformation of the multipole–multipole polarizabilities were achieved by comparisons between the Buckingham expansion in the traced and traceless forms. Considering the importance of the Buckingham expansion, we believe that a revisit of it is needed in order to clarify some of its ambiguities. In this study, we give a complete derivation of the Buckingham expansion, which we think is easily understood and more closely resembles its original form, as we revisit this important and interesting topic.

In this study, the derivation is based solely on Cartesian tensors, because they are more relevant to the experimentally reported molecular multipoles and (hyper)polarizabilities. The transformation between Cartesian representation and spherical representation with solid harmonic spherical bases has been well documented [2, 11]. In section 2 we derive the Buckingham expansion in the traced form, using Taylor series, with necessary discussions on the Buckingham convention according to the original Buckingham expansion in the traceless form. We next propose an auxiliary traced field gradient, from which we derive the Buckingham expansion in the traced form in section 3. By using this method, we can easily obtain the transformation from traced multipoles and (hyper)polarizabilities to their corresponding traceless counterparts. While the former is well known, the latter may not be trivial without the auxiliary traced field gradient. Additionally, we demonstrate that the traceless features of multipoles as well as the multipole–multipole polarizabilities, are consequences of the Laplace equation. In section 4, we apply the finite field method to high-level \textit{ab initio} calculations, utilizing the Buckingham expansion, to numerically calculate the dipole polarizability, quadrupole and quadrupole–quadrupole polarizability of carbon dioxide. In appendix A, we briefly summarize previous derivations, especially McLean and Yoshimine’s derivation [12], and derive the conversions of the multipole–multipole polarizabilities of different conventions. In appendix B, we propose a general Buckingham expansion in the traced form and derive the finite difference expressions of the traced quadrupole and quadrupole–quadrupole polarizability with accuracy of \( O(E^4) \). Note that the derivation of any multipole or (hyper)polarizability is straightforward using the finite field method in appendix B, and the transformations from the traced quadrupole and quadrupole–quadrupole polarizability to the corresponding traceless counterparts are derived in section 3. In appendix C, we propose a general formula for the Buckingham expansion in the traceless form based on the discussions in the text.

2. The Buckingham expansion in the traced form

Considering the interaction of a charge distribution \( \rho(r) \), centered at the origin \( O \) of a Cartesian coordinate system, with an external electrostatic perturbation, the external electrostatic potential at \( r \) can be expanded via Taylor series around \( O \), i.e. \([2, 12]\):

\[
\varphi(r) = \varphi(0) - r_\alpha E_\alpha - \frac{1}{2} r_\alpha r_\beta E_{\alpha\beta} - \frac{1}{6} r_\alpha r_\beta r_\gamma E_{\alpha\beta\gamma} - \frac{1}{24} r_\alpha r_\beta r_\gamma r_\delta E_{\alpha\beta\gamma\delta} - \cdots, \tag{1}
\]

in which \( \varphi, E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma} \) and \( E_{\alpha\beta\gamma\delta} \) denote external electric potential, field, gradients, etc, and the Greek subscripts denote the Cartesian coordinate component \( \{x, y, z\} \). In equation (1), Einstein summation convention on the repeated subscripts is adopted throughout.

Using equation (1), the interaction between \( \rho(r) \) and the externally perturbing \( \varphi(r) \) is given by [2]:

\[
U - U_0 = \int_\mathcal{V} d\mathbf{r} \rho(\mathbf{r}) \varphi(\mathbf{r}) = q \varphi - \mu'_\alpha E_\alpha - \frac{1}{2} Q'_{\alpha\beta} E_{\alpha\beta} - \frac{1}{6} O'_{\alpha\beta\gamma} E_{\alpha\beta\gamma} - \frac{1}{24} H'_{\alpha\beta\gamma\delta} E_{\alpha\beta\gamma\delta} - \cdots, \tag{2}
\]

in which \( U_0 \) is the energy without external field perturbations, and \( q, \mu'_\alpha, Q'_{\alpha\beta}, O'_{\alpha\beta\gamma}, \) and \( H'_{\alpha\beta\gamma\delta} \) are monopole (charge), dipole, traced quadrupole, traced octopole and traced hexadecapole, respectively, i.e.:

\[
q = \int_\mathcal{V} d\mathbf{r} \rho(\mathbf{r}) \tag{3a}
\]

\[
\mu'_\alpha = \int_\mathcal{V} d\mathbf{r} \rho(\mathbf{r}) r_\alpha \tag{3b}
\]
\[ Q'_{\alpha\beta} = \int_V d\nu p(r) r_\alpha r_\beta \]  \hspace{1cm} (3c) \\
\[ O'_{\alpha\beta\gamma} = \int_V d\nu p(r) r_\alpha r_\beta r_\gamma \]  \hspace{1cm} (3d) \\
\[ H'_{\alpha\beta\gamma\delta} = \int_V d\nu p(r) r_\alpha r_\beta r_\gamma r_\delta \]  \hspace{1cm} (3e)

Equation (3) stands because the external electrostatic perturbations, \( \varphi, E_{\alpha\beta}, E_{\alpha\beta\gamma}, E_{\alpha\beta\gamma\delta}, \) etc, are independent of \( r \) and the integration is performed over the entire space \( V \) occupied by \( p(r) \), which is well separated from the external source. The primes on the superscripts of the multipoles in equations (2) and (3) remind us that they may all be inducible if \( \rho(r) \) is polarizable, i.e.:

\[ \mu'_{\alpha} = \mu_{\alpha} + \mu_{\alpha}^{\text{ind}}, \quad Q'_{\alpha\beta} = Q_{\alpha\beta} + Q_{\alpha\beta}^{\text{ind}}, \]
\[ O'_{\alpha\beta\gamma} = O_{\alpha\beta\gamma} + O_{\alpha\beta\gamma}^{\text{ind}}, \ldots, \]

(4) in which \( \mu_{\alpha}, Q_{\alpha\beta}, \) and \( O_{\alpha\beta\gamma} \) are the permanent multipoles, with the superscript ‘ind’ in the second term on the RHS denotes the individually inducible counterpart. Such classification is subtle, because the inducible terms only appear with additional external perturbations. Otherwise, they are the permanent multipoles. Since there is no charge source or sink other than \( \rho(r) \), they are permanent and not inducible.

With additional external perturbation, the multipoles can be expanded, again, via Taylor series, i.e.:

\[ \mu'_{\alpha} = -\frac{\partial U}{\partial E_{\alpha\beta}} = \mu_{\alpha} + a_{\alpha\beta} E_{\beta} + \frac{1}{2} a'_{\alpha\beta\gamma} E_{\beta} E_{\gamma} + \ldots \]
\[ Q'_{\alpha\beta} = -2 \frac{\partial U}{\partial E_{\beta\delta}} = Q_{\alpha\beta} + a'_{\alpha\beta\gamma} E_{\gamma} + \frac{1}{2} \left( c'_{\alpha\beta\gamma\delta} + c'_{\beta\alpha\gamma\delta} \right) E_{\gamma} E_{\delta} + \ldots \]
\[ O'_{\alpha\beta\gamma} = -6 \frac{\partial U}{\partial E_{\beta\gamma\delta}} = O_{\alpha\beta\gamma} + d'_{\alpha\beta\gamma\delta} E_{\delta} + \frac{1}{2} g'_{\beta\alpha\delta\gamma\delta} E_{\delta} E_{\gamma} + \ldots \]
\[ H'_{\alpha\beta\gamma\delta} = -24 \frac{\partial U}{\partial E_{\beta\gamma\delta\delta}} = H_{\alpha\beta\gamma\delta} + \ldots, \]

(5a)

in which all but the first term on the RHS are the induced multipoles by the external electric field and gradients. \( a_{\alpha\beta\gamma} \) is dipole polarizability, \( a_{\alpha\beta\gamma\delta} \) is dipole–quadrupole polarizability, \( d_{\alpha\beta\gamma\delta} \) is dipole–octopole polarizability, \( c_{\alpha\beta\gamma\delta} \) is quadrupole–quadrupole polarizability, \( g_{\beta\alpha\delta\gamma\delta} \) is quadrupole–octopole polarizability and \( p_{\beta\alpha\delta\gamma\delta} \) is octopole–octopole polarizability, respectively, which are:

\[ a_{\alpha\beta\gamma} = \frac{\partial \mu_{\beta}}{\partial E_{\alpha\beta}} = -\frac{\partial^2 U}{\partial E_{\alpha\beta} \partial E_{\beta}} \]  \hspace{1cm} (6a) \\
\[ a_{\gamma\alpha\beta\delta} = 2 \frac{\partial \mu_{\beta\gamma}}{\partial E_{\alpha\beta\delta}} = \frac{\partial Q_{\alpha\beta\delta}}{\partial E_{\beta}} = -2 \frac{\partial^2 U}{\partial E_{\alpha\beta\delta} \partial E_{\beta}} \]  \hspace{1cm} (6b) \\
\[ d_{\beta\gamma\alpha\delta} = 6 \frac{\partial \mu_{\beta\gamma}}{\partial E_{\beta\gamma\delta}} = \frac{\partial Q_{\beta\alpha\delta}}{\partial E_{\delta}} = -6 \frac{\partial^2 U}{\partial E_{\beta\gamma\delta} \partial E_{\delta}} \]  \hspace{1cm} (6c) \\
\[ c_{\gamma\alpha\beta\delta} = 2 \frac{\partial Q_{\alpha\beta\delta}}{\partial E_{\gamma}} = -2 \frac{\partial^2 U}{\partial E_{\alpha\beta\delta} \partial E_{\gamma}} \]  \hspace{1cm} (6d) \\
\[ g_{\beta\alpha\delta\gamma\delta} = 6 \frac{\partial Q_{\beta\alpha\delta\gamma}}{\partial E_{\delta}} = 2 \frac{\partial Q_{\beta\alpha\delta\gamma}}{\partial E_{\delta}} = -12 \frac{\partial^2 U}{\partial E_{\beta\alpha\delta\gamma} \partial E_{\delta}} \]  \hspace{1cm} (6e) \\
\[ p_{\beta\alpha\delta\gamma\delta} = 3 \frac{\partial Q_{\beta\alpha\delta\gamma\delta}}{\partial E_{\delta}} = -18 \frac{\partial^2 U}{\partial E_{\beta\alpha\delta\gamma\delta} \partial E_{\delta}}, \]

(6f)

in which the multipole–multipole polarizabilities are all in the traced form. The primes on the superscripts of the (hyper) polarizabilities in equation (5) denote that they may all be inducible upon additional external perturbation. For example:

\[ a'_{\alpha\beta\gamma} = a_{\alpha\beta\gamma} + b'_{\alpha\beta\gamma} E_{\gamma} + \frac{1}{2} c_{\gamma\alpha\beta\delta} E_{\delta} + \ldots \]
\[ b'_{\alpha\beta\gamma} = b_{\alpha\beta\gamma} + c'_{\gamma\alpha\beta\delta} E_{\delta} + \ldots \]
\[ c'_{\gamma\alpha\beta\delta} = a_{\gamma\alpha\beta\delta} + b'_{\gamma\alpha\beta\delta} E_{\delta} + \frac{1}{2} c_{\gamma\beta\alpha\delta\gamma} E_{\delta} + \ldots \]

(7a)

in which \( b_{\alpha\beta\gamma} \) and \( c_{\gamma\alpha\beta\delta} \) are the first and second dipole hyperpolarizability, respectively, \( b_{\alpha\beta\gamma} \) is dipole–dipole–quadrupole polarizability, and \( c_{\gamma\alpha\beta\delta} \) is dipole–quadrupole–quadrupole polarizability, which are:

\[ b_{\beta\gamma\alpha\delta} = \frac{\partial a_{\alpha\beta\gamma}}{\partial E_{\delta}} = -\frac{\partial^3 U}{\partial E_{\alpha\beta\gamma} \partial E_{\delta}} \]  \hspace{1cm} (8a) \\
\[ c_{\gamma\alpha\beta\delta} = \frac{\partial a_{\alpha\beta\gamma}}{\partial E_{\delta}} = -\frac{\partial^3 U}{\partial E_{\alpha\beta\gamma} \partial E_{\delta}} \]  \hspace{1cm} (8b) \\
\[ b_{\gamma\alpha\beta\delta} = \frac{2}{3} \frac{\partial a_{\alpha\beta\gamma}}{\partial E_{\delta}} = -2 \frac{\partial^3 U}{\partial E_{\alpha\beta\gamma} \partial E_{\delta}} \]  \hspace{1cm} (8c) \\
\[ c_{\gamma\alpha\beta\delta} = \frac{2}{3} \frac{\partial a_{\alpha\beta\gamma}}{\partial E_{\delta}} = -2 \frac{\partial^3 U}{\partial E_{\alpha\beta\gamma} \partial E_{\delta}}. \]

(8d)

In the Taylor series in equations (5) and (7), the Greek subscripts of the multipole–multipole polarizabilities are grouped, with different groups separated by a comma. The convention in this study is that the subscripts in the same group are permutable, while the exchange of the groups of the subscripts separated by a comma is not allowed. Thus, the singly grouped subscripts of electric fields, gradients, multipoles and dipole (hyper)polarizabilities are permutable. For the multiply grouped subscripts, taking dipole–quadrupole polarizability as example, \( a_{\gamma\alpha\beta\delta} \) and \( a_{\gamma\alpha\beta\delta} \) are allowed in the summation of equations (5a)–(5b), but \( a_{\gamma\alpha\beta\delta} \) and \( a_{\gamma\alpha\beta\delta} \) are not, although the four terms are all equal. Thus, such non-exchangeable group convention includes 27 \( a_{\gamma\alpha\beta\delta} \) terms in
total, while allowing group exchange of \(a_{\alpha/\beta} \gamma\) merely doubles the number of terms, with the values of the terms of the former two times the corresponding terms of the latter. A similar argument also applies to \(b_{\gamma/\alpha/\beta} \delta\) \(d_{\delta/\alpha/\beta} \gamma\), \(e_{\gamma/\alpha/\beta} \delta\), etc. On the other hand, it is notable that the groups of the subscripts of \(c_{\alpha/\beta} \gamma\), \(p_{\alpha/\beta} \gamma\), etc. with same number of subscripts in some groups, are inherently exchangeable. Thus, they are explicitly included in equations (5b)–(5c). The same argument also accounts for the \(c_{\gamma/\alpha/\beta} \delta\) in equation (7c), because the groups, \(\alpha/\beta\) and \(\delta\), in the subscripts of \(c_{\gamma/\alpha/\beta} \delta\) are inherently exchangeable. Generally, if there are \(n\) inherently exchangeable groups in the subscripts of a multipole–multipole polarizability, the factor on the corresponding term is \(n!\) to account for the permutations of the inherently exchangeable groups.

It should be noted that the above convention was implicitly adopted by the Buckingham expansion in its originally proposed form [3–5], and we thus call it the Buckingham convention hereafter. Other conventions are also adopted in literatures [12–14]. Since the Buckingham expansion has been widely adopted in the community when reporting the multipole–multipole polarizabilities [8, 9, 11], other conventions are often converted to the Buckingham convention. One conversion between two different conventions is given in appendix A. Moreover, the Buckingham convention leads to a simple generalized Buckingham expansion in the traced form, as shown in appendix B.

Though the above Taylor series can be continued toward infinite terms, we hopefully include in equations (5)–(8) most of the important ones. The induced multipoles and (hyper) polarizabilities can then be obtained via successive integrations in a reversible manner [13]. For example, the induced component of the dipole polarizability \(\alpha_{\alpha/\beta}\) on external fields \(E_\alpha\) and \(E_\beta\) from equation (7b), is:

\[
\alpha'_{\alpha/\beta} - \alpha_{\alpha/\beta} = \int_0^E \beta_{\alpha/\beta} \lambda d(\lambda E_\gamma) = \int_0^E (\beta_{\alpha/\beta} + \gamma_{\alpha/\beta} \lambda E_\gamma + \cdots) E_\gamma d\lambda = \beta_{\alpha/\beta} E_\gamma + \frac{1}{2} \gamma_{\alpha/\beta} E_\gamma E_\delta + \cdots. \tag{9}
\]

For the second dipole hyperpolarizability \(\gamma_{\alpha/\beta} \delta\) in the final expression in equation (9), the factor 1/2 arises from the integration over the parameter \(\lambda(0 \leq \lambda \leq 1)\) for a reversible polarization process [13]. Feeding the induction component of \(\alpha_{\alpha/\beta}\) in equation (9) back to equation (7a), we have:

\[
\alpha'_{\alpha/\beta} = \alpha_{\alpha/\beta} + \beta_{\alpha/\beta} E_\gamma + \frac{1}{2} \gamma_{\alpha/\beta} E_\gamma E_\delta + \cdots, \tag{7a'}
\]

which gives the differential dipole polarizability [6] \(\alpha_{\alpha/\beta}\) on external \(E_\alpha\), \(E_\beta\), and \(E_\delta\). Integrating equation (7a') over \(E_\beta\) and equation (7c) over \(E_\delta\) with the reversible polarization process, respectively, and avoiding the double counting on the term involving dipole–dipole–quadrupole polarizability \(b_{\alpha/\beta/\gamma}\), we can obtain the induced dipole \(\mu'_{\alpha}\), i.e.:

\[
\mu'_{\alpha} = \int_0^\gamma \left( \alpha_{\alpha/\beta} + \beta_{\alpha/\beta} \lambda E_\delta + \frac{1}{2} \gamma_{\alpha/\beta} \lambda E_\delta E_\delta + \cdots \right) E_\delta d\lambda + \frac{1}{2} \int_0^\gamma \left( a_{\alpha/\beta} + b'_{\alpha/\beta} \lambda E_\delta + c_{\alpha/\beta} \lambda E_\delta E_\delta + \cdots \right) E_\delta d\lambda = \alpha_{\alpha/\beta} E_\delta + \frac{1}{2} \beta_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{6} \gamma_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots + \frac{1}{2} a_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{2} b'_{\alpha/\beta} E_\delta E_\gamma + \cdots + \frac{1}{4} c_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots \tag{10a}
\]

\[
Q'_{\alpha/\beta} = \int_0^\gamma \left( a_{\alpha/\beta} + b'_{\alpha/\beta} \lambda E_\delta + c_{\alpha/\beta} \lambda E_\delta E_\delta + \cdots \right) E_\delta d\lambda = a_{\alpha/\beta} E_\gamma + \frac{1}{2} b'_{\alpha/\beta} E_\gamma E_\delta + \frac{1}{4} c_{\alpha/\beta} E_\gamma E_\delta + \cdots \tag{10b}
\]

Feeding equation (10a) back to equations (5a), and (10b) to equation (5b), we have:

\[
\mu'_{\alpha} = \mu_{\alpha} + \alpha_{\alpha/\beta} E_\delta + \frac{1}{2} \beta_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{6} \gamma_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots + \frac{1}{2} a_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{2} b'_{\alpha/\beta} E_\delta E_\gamma + \cdots + \frac{1}{4} c_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots \tag{5a'}
\]

\[
Q'_{\alpha/\beta} = Q_{\alpha/\beta} + a_{\alpha/\beta} E_\gamma + \frac{1}{2} b'_{\alpha/\beta} E_\gamma E_\delta + \frac{1}{4} c_{\alpha/\beta} E_\gamma E_\delta + \cdots \tag{5b'}
\]

The Buckingham expansion in the traced form can be obtained via successive integration of equations (5a)–(5d), with equations (5a)–(5b) replaced by equations (5a')–(5b'). Thus:

\[
U - U_0 = -\int_0^\gamma \mu'_{\alpha} E_\delta d\lambda = -\left( \mu_{\alpha} + \frac{1}{2} \alpha_{\alpha/\beta} E_\delta + \frac{1}{3!} \beta_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{4!} \gamma_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots \right) E_\delta + \frac{1}{2} a_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{2} b_{\alpha/\beta} E_\delta E_\gamma + \frac{1}{4} c_{\alpha/\beta} E_\delta E_\gamma E_\delta + \cdots \tag{11a}
\]
\[ U - U_0 = \frac{1}{2} \int \Omega_{\alpha\beta} E_{\alpha\beta} \, d\lambda \]
\[ = -\frac{1}{2} \left[ O_{\alpha\beta \delta} + a_{\gamma,\alpha,\beta} E_\gamma + \frac{1}{2} b_{\delta,\alpha,\beta} E_\delta + \frac{1}{2} c_{\gamma,\delta,\alpha,\beta} E_\gamma E_\delta \right. \]
\[ + \frac{1}{2} \left( d_{\delta,\alpha,\beta,\gamma} E_\delta E_\gamma + \frac{1}{2} e_{\delta,\gamma,\alpha,\beta} E_\delta E_\gamma \right) \]
\[ + \frac{1}{3!} g_{\delta,\gamma,\alpha,\beta} E_\delta E_\gamma + \cdots \right] E_{\alpha\beta} \]
\[ U - U_0 = -\frac{1}{6} \int \Omega_{\alpha\beta \delta} E_{\alpha\beta \delta} \, d\lambda \]
\[ = -\frac{1}{6} \left[ H_{\alpha\beta \delta} + \frac{1}{2} h_{\gamma,\alpha,\beta,\delta} E_\gamma E_\delta + \cdots \right] E_{\alpha\beta} \]
\[ : \]
in which the primes on the superscripts are dropped in the final expression, because they are permanent ones without additional external electric fields or gradients other than those listed in the otherwise presented ones. With such understanding, the superscript primes are hereafter dropped. Using equations (11), equation (2) can be further expanded to include both multipoles and (hyper)polarizabilities. Summing equation (11) and skipping the same terms to avoid double count, we can expand the energy of a polarizable charge distribution. The resultant expansion is the Buckingham expansion in the traced form, i.e.:
\[ U = U_0 + q \varphi \]
\[ - \left( \mu_\alpha E_\alpha + \frac{1}{2} \beta_\alpha E_\alpha E_\alpha + \frac{1}{6} \alpha_\alpha E_\alpha + \cdots \right) \]
\[ - \frac{1}{2} \left[ O_{\alpha\beta \delta} + a_{\gamma,\alpha,\beta} E_\gamma + \frac{1}{2} b_{\delta,\alpha,\beta} E_\delta + \frac{1}{2} c_{\gamma,\delta,\alpha,\beta} E_\gamma E_\delta \right. \]
\[ + \frac{1}{2} \left( d_{\delta,\alpha,\beta,\gamma} E_\delta E_\gamma + \frac{1}{2} e_{\delta,\gamma,\alpha,\beta} E_\delta E_\gamma \right) \]
\[ + \frac{1}{3!} g_{\delta,\gamma,\alpha,\beta} E_\delta E_\gamma + \cdots \right] E_{\alpha\beta \delta} \]
\[ \cdots \]
\[ (12) \]

From equation (12), we can deduce that for a polarizable charge distribution the Buckingham expansion in the traced form can be constructed via successive Taylor series toward infinite terms, and all the multipoles in equation (4) and the multipole–multipole polarizabilities in equations (6) and (8) are the traced ones. Note that the Buckingham convention is adopted throughout the derivation. In appendix B, we give the general formula for the complete Buckingham expansion in the traced form. In the actual numerical calculations, it is convenient to get the traced multipoles and polarizabilities, and then transform them to their traceless counterparts if needed, as discussed below.

3. The Buckingham expansion in the traceless form

Without losing generality, we consider the externally perturbed \( \varphi \) is generated by a test positive unit electron charge \( e \) at \( \mathbf{R} \) far from \( O \) on which the charge distribution \( \rho(r) \) is located. The electrostatic potential at \( r \) due to \( e \) at \( \mathbf{R} \) is\( \varphi(r) = e/|\mathbf{R} - r| \), which, upon binomial expansion with respect to \( O \), is:
\[ \varphi(r) = e \left( \frac{1}{R} + r_\alpha \frac{\partial R_{-1}}{\partial R_\alpha} - \frac{2}{3} r_\alpha r_\beta \frac{\partial^2 R_{-1}}{\partial R_\alpha \partial R_\beta} + \cdots \right) \]
\[ + \frac{1}{3!} r_\alpha r_\beta r_\gamma \frac{\partial^3 R_{-1}}{\partial R_\alpha \partial R_\beta \partial R_\gamma} + \cdots \] (13)
Comparing equation (13) with equation (1), we have the external potential, electric field, and gradients at \( O \), due to \( e \) at \( \mathbf{R} \), i.e.:
\[ \varphi(0) = \frac{e}{R} \] (14a)
\[ E_\alpha = -e \frac{\partial \varphi}{\partial R_\alpha} = \frac{e}{R^3} \] (14b)
\[ E_{\alpha\beta} = e \frac{\partial^2 \varphi}{\partial R_\alpha \partial R_\beta} = e \frac{1}{R^5} (3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) \] (14c)
\[ E_{\alpha\beta \delta} = -e \frac{\partial^3 \varphi}{\partial R_\alpha \partial R_\beta \partial R_\delta} \]
\[ = e \frac{1}{R^7} \left[ 15R_\alpha R_\beta R_\delta - 3R^2 \right. \]
\[ \times \left( R_\alpha \delta_{\beta\gamma} + R_\beta \delta_{\alpha\gamma} + R_\gamma \delta_{\alpha\beta} \right) \] (14d)
\[ E_{\alpha\beta \delta} = e \frac{\partial^4 \varphi}{\partial R_\alpha \partial R_\beta \partial R_\delta} \]
\[ = e \frac{1}{R^9} [105R_\alpha R_\beta R_\delta R_\gamma + \cdots] \]
\[ - 15R^2 (R_\alpha R_\beta \delta_{\gamma\delta} + R_\alpha R_\delta \delta_{\gamma\beta} + R_\beta R_\delta \delta_{\alpha\gamma} + R_\gamma R_\delta \delta_{\alpha\beta}) \]
\[ + R_\alpha R_\beta \delta_{\gamma\delta} + R_\gamma R_\delta \delta_{\alpha\beta} \]
\[ + 3R^4 (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \] (14e)
\[ \cdots \]
over \(\{x, y, z\}\), because \(O\) and \(R\) are spatially well separated and the Laplace equation is satisfied on any place other than \(R\) where \(\epsilon\) is located \([2, 4, 12]\). We next define auxiliary external electric field gradients in the traced form, \(F_{\alpha,\beta}, F_{\alpha,\gamma}, F_{\alpha,\gamma\delta}\), with the aid of equations (14c)–(14e), i.e.:

\[
F_{\alpha,3} = \epsilon \frac{3R_{\mu}R_{\beta}}{R^3}
\]

(15a)

\[
F_{\alpha,3} = \epsilon \frac{15R_{\mu}R_{\beta}R_{\gamma}}{R^5}
\]

(15b)

\[
F_{\alpha,\gamma\delta} = \epsilon \frac{105R_{\mu}R_{\nu}R_{\rho}R_{\sigma}}{R^9}.
\]

(15c)

Since electric field \(E_{\alpha}\) is vector, it does not possess a ‘trace’. Using equation (15), the electric field gradients in equations (14c)–(14e) can be written as:

\[
E_{\alpha,3} = F_{\alpha,3} - \frac{1}{3} \epsilon R_{\mu}R_{\beta}F_{\alpha,\mu}\beta
\]

(16a)

\[
E_{\alpha,\gamma} = F_{\alpha,\gamma} - \frac{1}{5} \left( F_{\alpha,\mu\nu} \delta_{\gamma\nu} + F_{\mu,\nu\gamma} \delta_{\mu\alpha} + F_{\mu,\gamma\nu} \delta_{\mu\alpha} \right)
\]

(16b)

\[
E_{\alpha,\gamma\delta} = F_{\alpha,\gamma\delta} - \frac{1}{7} \left( F_{\mu,\nu\rho\gamma} \delta_{\delta\gamma\rho} + F_{\mu,\rho\gamma\nu} \delta_{\delta\rho\gamma} + F_{\mu,\gamma\nu\rho} \delta_{\delta\rho\gamma} \right)
\]

(16c)

in which the places of the subscripts \(\alpha, \beta, \gamma, \delta\) on the RHS are consistent with those on the LHS, which represents a specific Cartesian component of electric field or gradient. Equation (16) is derived by using the identity \(R^2 = R_{\mu}R_{\mu} = R_{\alpha}^2 + R_{\beta}^2 + R_{\gamma}^2 + R_{\delta}^2\), since the subscript \(\mu \in \{x, y, z\}\) is dummy, and similarly \(R^4 = R_{\mu}R_{\nu}R_{\rho}R_{\sigma} = R_{\alpha\beta\gamma\delta}^2\), in which the subscripts \(\mu\) and \(\nu\) are both dummy. It is easy to verify the traceless feature of electric field gradients by either using equations (14c)–(14e), or, equivalently, using equation (16), i.e.:

\[
E_{\alpha,\alpha} = 0
\]

(17a)

\[
E_{\alpha,\alpha} = E_{\alpha,\alpha} = E_{\alpha,3} = 0
\]

(17b)

\[
E_{\alpha,\gamma\delta} = E_{\alpha,\alpha} = E_{\alpha,\beta} = E_{\alpha,\gamma\gamma} = 0.
\]

(17c)

For the above identities, equation (17a) is obtained via equation (16a), i.e. \(E_{\alpha,\alpha} = F_{\alpha,3} - \frac{1}{3} \epsilon R_{\mu}R_{\beta}F_{\alpha,\mu}\beta = 0\), using the identity \(\delta_{\alpha\alpha}\) for the repeated dummy subscript \(\alpha\). Using the first identity \(E_{\alpha,\alpha}\) in equation (17b) as example, we have from equation (16b):

\[
E_{\alpha,\alpha} = F_{\alpha,\alpha} - \frac{1}{5} \left( F_{\mu,\nu\rho\gamma} \delta_{\alpha\gamma\rho} + F_{\mu,\rho\gamma\nu} \delta_{\alpha\rho\gamma} + F_{\mu,\gamma\nu\rho} \delta_{\alpha\rho\gamma} \right)
\]

(17b)

\[
E_{\alpha,\alpha} = F_{\alpha,\alpha} - \frac{1}{5} \left( F_{\mu,\nu\rho\gamma} + F_{\nu,\rho\gamma\nu} + 3F_{\mu,\gamma\nu\rho} \right) = 0,
\]

in which we use the fact that the repeated subscript \(\alpha\) is dummy, so that \(\delta_{\alpha\alpha} = 3\) and \(\alpha\) can be replaced by another dummy variable \(\mu\), i.e. \(F_{\alpha,\mu\nu} = F_{\mu,\nu\gamma}\). Additionally, \(F_{\mu,\nu\rho\gamma} = F_{\nu,\rho\gamma\mu}\). Since \(F_{\alpha,\beta}\) is invariant upon the permutation of the subscripts. Similar arguments apply on the other identities in equations (17b)–(17c).

The traceless feature of the electric field gradients imposes the traceless condition on the corresponding multipoles. Taking, again, \(E_{\alpha,\beta}\) as an example, and feeding \(E_{\alpha,\beta}\) in equation (16a) to the corresponding trace quadrupole \(Q_{\alpha,\beta}\) contribution to the energy in equation (2), we have \(-\frac{1}{2} Q_{\alpha,\beta} \frac{d\Theta_{\alpha,\beta}}{d\alpha}\) is dummy, the last term can be written as:

\[
\frac{1}{2} Q_{\alpha,\beta} \frac{d\Theta_{\alpha,\beta}}{d\alpha} = \frac{1}{2} \left( \frac{\Theta_{\alpha,\beta}}{\frac{1}{3} Q_{\alpha,\beta}} - \frac{1}{3} Q_{\alpha,\beta} Q_{\alpha,\beta} F_{\alpha,\mu}\beta \right)
\]

(17)

Thus, \(\theta_{3,\beta} = Q_{\alpha,\beta} - \frac{1}{2} \frac{d^2}{d\Theta_{\alpha,\beta}^2}\) on the RHS of equation (18) is traceless, i.e. \(\Theta_{\alpha,\beta} = 0\), for the same reasoning in equation (17). Thus, \(\theta_{3,\beta}\) can be defined as the traceless quadrupole. On the other hand, such definition is not unique, because the traceless feature is maintained upon multiplication of any factor \(f_0\), i.e. \(f_0 \theta_{3,\beta}\). The Gaussian package \([15]\) apparently adopts \(f_0 = 1\), while in nuclear physics it adopts \(f_0 = 3\) \([16]\). Here, we adopt Buckingham’s definition with \(f_0 = 3/2\), so that the traceless quadrupole is defined to be \([4]\):

\[
\Theta_{\alpha,\beta} = f_0 \theta_{3,\beta} = \frac{1}{2} \left( \frac{1}{3} Q_{\alpha,\beta} - Q_{\alpha,\beta} Q_{\alpha,\beta} F_{\alpha,\mu}\beta \right).
\]

(19)

Thus, the traced \(Q_{\alpha,\beta}\) in equation (3c) can be transformed to the traceless \(\Theta_{\alpha,\beta}\) with the above equation. Using equation (19) with \(f_0 = 3/2\), the energy \(-\frac{1}{2} Q_{\alpha,\beta} E_{\alpha,\beta}\), in the presence of solely external electric field gradient, needs to be scaled by \(\frac{1}{f_0} = \frac{2}{3}\). Using equations (11b), (18) and (19), we have:

\[
U - U_0 = -\frac{1}{2} Q_{\alpha,\beta} E_{\alpha,\beta} = -\frac{1}{2} f_0 \theta_{3,\beta} F_{\alpha,\beta} - \frac{1}{3} \Theta_{\alpha,\beta} E_{\alpha,\beta}.
\]

(20)

The validation of last expression of equation (20) is due to the traceless feature of \(E_{\alpha,\beta}\) and \(\Theta_{\alpha,\beta}\). Using equation (16a) and identity \(\Theta_{\alpha,\alpha} = 0\), the energy in external electric field gradient is:

\[
-\frac{1}{3} \Theta_{\alpha,\beta} E_{\alpha,\beta} = -\frac{1}{3} \Theta_{\alpha,\beta} \left( F_{\alpha,\beta} - \frac{1}{3} F_{\mu,\nu\gamma} \delta_{\alpha\beta} \right)
\]

(20a)

\[
= -\frac{1}{3} \Theta_{\alpha,\beta} F_{\alpha,\beta} + \frac{1}{9} \Theta_{\alpha,\beta} F_{\mu,\nu\gamma} - \frac{1}{3} \Theta_{\alpha,\beta} F_{\alpha,\beta}.
\]

The above relation validates the last expression of equation (20).

From equation (20), we can see that it is equivalent to use the traced \(Q_{\alpha,\beta}\) with traceless \(E_{\alpha,\beta}\) in equation (14c) or equation (16a), or to use traceless \(\Theta_{\alpha,\beta}\) with the auxiliary traced \(F_{\alpha,\beta}\) in equation (15a). On the other hand, using both traceless multipole and traceless electric field gradient is redundant. With such understanding, from \(Q_{\alpha,\beta} = -\frac{2}{3} \frac{d\Theta}{d\alpha}\), we see that when the charge distribution \(\rho(r)\) senses a variation of
the traceless $F_{\alpha\beta}$, it feeds back the traced $Q_{\alpha\beta}$ in response. In contrast, equation (20) also tells that $\Theta_{\alpha\beta} = -3\frac{\partial \phi}{\partial \alpha\beta}$. Thus, when the charge distribution $\rho(r)$ senses a variation of the traced $F_{\alpha\beta}$, it feeds back the traceless $\Theta_{\alpha\beta}$ in response. Using equation (16a), we have:

$$J_{\gamma,\alpha\beta} = \frac{\partial E_{\gamma}}{\partial F_{\alpha\beta}} = \frac{\partial F_{\delta}}{\partial F_{\alpha\beta}} \frac{1}{3} \frac{\partial F_{\mu\nu}}{\partial F_{\alpha\beta}} \delta_{\delta} = \delta_{\alpha\beta} \delta_{\gamma} - \frac{1}{3} \delta_{\alpha\beta} \delta_{\gamma},$$

(21a)

in which $\frac{\partial F_{\delta}}{\partial F_{\alpha\beta}} = \delta_{\mu\nu} \delta_{\beta} = \delta_{\alpha\beta}$ is used. The traceless quadrupole, $\Theta_{\alpha\beta}$, can then be calculated, equivalently, via:

$$\Theta_{\alpha\beta} = -\frac{1}{2} \frac{\partial U}{\partial \alpha\beta} = \frac{1}{2} \frac{\partial U}{\partial E_{\alpha\beta}} = \frac{1}{2} \frac{\partial U}{\partial E_{\alpha\beta}} \frac{1}{3} \frac{\partial F_{\mu\nu}}{\partial F_{\alpha\beta}} \delta_{\delta} = \frac{1}{3} \delta_{\alpha\beta} \delta_{\gamma},$$

(22a)

in which $Q_{\alpha\beta} = -2\frac{\partial U}{\partial E_{\alpha\beta}}$, as in equation (5b), and $f_{\alpha} = 3/2$ as suggested by Buckingham is adopted. Thus, equation (22a) gives the same traceless $\Theta_{\alpha\beta}$ in equation (19), as expected.

The differentiation of energy with respect to the auxiliary traced electric field gradient in equation (15a) makes it simple and consistent for the transformation from the traced multipoles and multipole–multipole polarizabilities to the corresponding traceless counterparts. From equations (16b)–(16c), we have:

$$J_{\delta,\alpha\beta} = \frac{\partial E_{\delta \gamma}}{\partial F_{\alpha\beta}} = \delta_{\delta \gamma} \delta_{\beta} = \delta_{\alpha\beta},$$

(21b)

$$J_{\gamma,\alpha\beta,\gamma} = \frac{\partial E_{\gamma \delta}}{\partial F_{\alpha\beta}} = \delta_{\gamma \delta} \delta_{\beta} = \delta_{\delta \gamma} \delta_{\alpha\beta} = \frac{1}{2} \left( \delta_{\alpha\beta} \delta_{\gamma} \delta_{\delta} + \delta_{\beta\gamma} \delta_{\delta} + \delta_{\gamma\delta} \delta_{\alpha\beta} \right),$$

(21c)

Similar to equation (22a) for transforming the traced $Q_{\alpha\beta}$ to the traceless $\Theta_{\alpha\beta}$, the traced octopole $O_{\alpha\beta\gamma}$ and hexadecapole $H_{\alpha\beta\gamma\delta}$ in equations (5c)–(5d) can be transformed to the traceless octopole $\Omega_{\alpha\beta\gamma}$ and hexadecapole $\Phi_{\alpha\beta\gamma\delta}$ with the aid of equations (21b)–(21c), i.e.:

$$\Omega_{\alpha\beta\gamma} = -f_{\beta} \frac{1}{2} \left( \frac{\partial U}{\partial Q_{\alpha\beta}} \left( \frac{1}{3} \frac{\partial F_{\mu\nu}}{\partial F_{\alpha\beta}} \delta_{\delta} \right) \right) = \frac{1}{2} \left( \zeta_{\alpha\beta\gamma} \delta_{\delta} - 3 \zeta_{\alpha\beta\gamma} \delta_{\delta} + \zeta_{\alpha\beta\gamma} \delta_{\delta} \right),$$

(22b)

$$\Phi_{\alpha\beta\gamma\delta} = -f_{\beta} \frac{1}{2} \left( \frac{\partial U}{\partial Q_{\alpha\beta}} \left( \frac{1}{3} \frac{\partial F_{\mu\nu}}{\partial F_{\alpha\beta}} \delta_{\delta} \right) \right) = \frac{1}{2} \left( \zeta_{\alpha\beta\gamma\delta} \delta_{\delta} - 3 \zeta_{\alpha\beta\gamma\delta} \delta_{\delta} + \zeta_{\alpha\beta\gamma\delta} \delta_{\delta} \right),$$

(22c)

In equations (22a)–(22c), the Buckingham factor of the transformation from traced $2^M$-moment to the traceless $2^M$-moment is:

$$f_{M} = \frac{(2M - 1)!!}{M!},$$

(23)

in which $!!$ denotes factorial and $!!$ denotes double factorial with $(2M - 1)!! = (2M - 1) \cdot (2M - 3) \cdots 1$. Thus, $f_{0} = \frac{5}{2}$ and $f_{\beta} = \frac{105}{24}$ are used in equations (22b) and (22c), respectively. If $\rho(r)$ is known, the traceless multipoles can be written explicitly using equations (3c)–(3e) and (22a)–(22c), i.e.:

$$\Theta_{\alpha\beta} = \frac{1}{2} \int dV \rho(r) \left( 3r_{\alpha} r_{\beta} - r^{2} \delta_{\alpha\beta} \right),$$

(24a)

$$\Omega_{\alpha\beta\gamma} = \frac{1}{6} \int dV \rho(r) \left[ 15r_{\alpha} r_{\beta} r_{\gamma} - 3r^{2} (r_{\alpha} \delta_{\beta\gamma} + r_{\beta} \delta_{\alpha\gamma} + r_{\gamma} \delta_{\alpha\beta}) \right],$$

(24b)

$$\Phi_{\alpha\beta\gamma\delta} = \frac{1}{24} \int dV \rho(r) \left[ 150r_{\alpha} r_{\beta} r_{\gamma} r_{\delta} - 15r^{2} (r_{\alpha} r_{\beta} \delta_{\gamma\delta} + r_{\alpha} r_{\gamma} \delta_{\beta\delta} + r_{\beta} r_{\gamma} \delta_{\alpha\delta} + r_{\gamma} r_{\delta} \delta_{\alpha\beta}) \right],$$

(24c)

Using the same reasoning as in equation (17), it can be verified by using either equation (22) or equation (24) for the following traceless identities:

$$\Theta_{\alpha\beta} = 0,$$

(25a)

$$\Omega_{\alpha\beta\gamma} = \Omega_{\alpha\gamma\beta} = \Omega_{\beta\alpha\gamma} = 0,$$

(25b)

$$\Phi_{\alpha\beta\gamma\delta} = \Phi_{\alpha\delta\beta\gamma} = \Phi_{\beta\alpha\gamma\delta} = \Phi_{\gamma\beta\delta\alpha} = \Phi_{\delta\gamma\alpha\beta} = 0,$$

(25c)
Though the transformation from the traced to the traceless multipoles is somehow tedious, the expression of energy is straightforward, as shown in equation (20) for the quadrupole. It can be seen that the energy would be the same by multiplying and then dividing $f_0$ in equation (23). Extending the equation (20), which is for the permanent quadrupole, to the corresponding inducible counterpart in equation (11b), we have:

$$U - U^0 = -\frac{1}{f_0} \left( f_0 Q_{\alpha\beta\gamma} + f_0 a_{\alpha\beta\gamma} E_\gamma + \frac{1}{2} f_0 b_{\alpha\beta\gamma\delta} E_\gamma E_\delta \right)$$

$$+ \frac{1}{2} f_0 C_{\gamma\alpha\beta\delta} E_\gamma E_\delta + \frac{1}{2} f_0 C_{\alpha\beta\gamma\delta} E_\gamma E_\delta$$

$$+ \frac{1}{3} f_0^3 f_{\alpha\beta\gamma} E_{\beta\gamma} + \cdots \right) E_{\alpha\beta\gamma}$$

$$= -\frac{1}{3} \left( \Theta_{\alpha\beta\gamma} + A_{\gamma\alpha\beta} E_\gamma E_\delta \right)$$

$$+ \frac{1}{2} B_{\alpha\beta\gamma\delta} E_\gamma E_\delta$$

$$+ \frac{1}{2} \Phi_{\gamma\alpha\beta\delta} E_\gamma E_\delta$$

$$+ \frac{1}{15} C_{\gamma\alpha\beta\delta} E_{\beta\gamma} + \cdots \right) E_{\alpha\beta\gamma}$$

(26a)

in which $f_0 = \frac{3}{2}$ and $f_0 = \frac{15}{6}$, according to equation (23), and $A_{\gamma\alpha\beta}$, $B_{\alpha\beta\gamma\delta}$, $C_{\alpha\beta\gamma\delta}$, $C_{\gamma\alpha\beta\delta}$, $G_{\alpha\beta\gamma\delta}$ denote the traceless multipole–multipole polarizabilities, with the corresponding lowercase symbols denote the traced counterparts. Thus, the way to convert the energy from the expression of the traced multipoles and (hyper)polarizabilities to the expression of the corresponding traceless counterparts is straightforward, i.e. by multiplying $f_0$ if electric field gradient $E_{\alpha\beta\gamma}$ is involved, and multiplying $f_1$ if electric field gradient $E_{\alpha\beta\gamma}$ is involved, etc. Such manipulation converts equation (11b) for the traced multipoles and multipole–multipole polarizabilities to the traceless counterparts in equation (26a). It is notable that for the terms involving quadrupole–quadrupole polarizability $C_{\alpha\beta\gamma\delta}$ and dipole–quadrupole–quadrupole polarizability $C_{\gamma\alpha\beta\delta}$, which have an inherently exchangeable group in the sub-indices, the corresponding $f_0$ is multiplied only once. This is because the corresponding traceless $\Theta_{\alpha\beta\gamma}$ and $A_{\gamma\alpha\beta}$ energy expressions are obtained by a single multiplication with $E_{\gamma\alpha\beta\delta}$ and both are converted to the traceless form, as discussed in equations (18)–(20). Moreover, it should be emphasized that equation (26a) merely denotes $-\frac{1}{2} Q_{\alpha\beta\gamma} E_{\alpha\beta\gamma} = -\frac{1}{3} \Theta_{\alpha\beta\gamma} E_{\alpha\beta\gamma}$ by extending equation (20) to include inducible quadrupoles contributed from various external electric fields and gradients, but cannot give the explicit form of the multipole–multipole polarizabilities. For example, equation (26a) denotes $-\frac{1}{2} C_{\gamma\alpha\beta\delta} E_{\alpha\beta\gamma} = -\frac{1}{2} C_{\gamma\alpha\beta\delta} E_{\alpha\beta\gamma}$ but cannot give the explicit form of $C_{\gamma\alpha\beta\delta}$ which will be derived below in equation (28).

Based on the above discussions regarding equation (26a), the contribution of the energy from the traceless octopole and hexadecapole, with inducible components can be extended from equations (11c)–(11d), i.e.:

$$U = U^0 = -\frac{1}{f_0^2} \left( f_0 Q_{\alpha\beta\gamma} + f_0 d_{\delta,\alpha\beta\gamma} E_\delta \right)$$

$$+ \frac{1}{2} f_0^2 f_{\alpha\beta\gamma\delta} E_{\beta\gamma} + \frac{1}{3} f_0^3 f_{\alpha\beta\gamma\delta} E_{\beta\gamma}$$

$$+ \frac{1}{15} f_0^4 f_{\alpha\beta\gamma\delta} E_{\beta\gamma} + \cdots \right) E_{\alpha\beta\gamma}$$

(26b)

$$U - U^0 = -\frac{1}{f_0} \left( f_0 H_{\alpha\beta\gamma} + \cdots \right) E_{\alpha\beta\gamma}$$

$$= -\frac{1}{105} \left( \Omega_{\alpha\beta\gamma} + D_{\gamma\alpha\beta} E_\delta + \cdots \right) E_{\alpha\beta\gamma}$$

(26c)

in which $D_{\gamma\alpha\beta}$ and $F_{\delta,\alpha\beta\gamma}$ are the dipole–octopole and octopole–octopole polarizabilities, respectively, in the traceless form. Note that since the groups of the subscripts of octopole–octopole polarizabilities are inherently exchangeable, the term involving it is multiplied by $f_0$ only once. Summing equations (26a)–(26c), and skipping the same terms to avoid double counts, the Buckingham expansion of the electrostatic energy of a polarizable charge distribution in the traced form, equation (12), can then be transform to the traceless form, i.e.:

$$U = U^0 + g \Phi$$

$$- \left( \mu_{\alpha\beta} E_\alpha + \frac{1}{2} \alpha_{\alpha\beta} E_\alpha E_\beta + \frac{1}{6} \beta_{\alpha\beta} E_\alpha E_\beta E_\gamma \right. $$

$$+ \frac{1}{24} \gamma_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma + \cdots \right)$$

$$- \frac{1}{3} \left( \Theta_{\alpha\beta\gamma} + A_{\gamma,\alpha\beta} E_\gamma + \frac{1}{2} B_{\delta,\alpha\beta} E_\gamma E_\delta + \cdots \right)$$

$$+ \frac{1}{2} \left( C_{\alpha\beta\gamma\delta} + C_{\gamma,\alpha\beta\delta} E_\gamma + \cdots \right) E_\beta + \cdots \right) E_{\alpha\beta\gamma}$$

$$- \frac{1}{15} \left( \Omega_{\alpha\beta\gamma} + D_{\delta,\alpha\beta\gamma} E_\delta + \frac{1}{3} G_{\delta,\alpha\beta\gamma} E_{\beta\gamma} + \cdots \right) E_{\alpha\beta\gamma}$$

(27)

Equation (27) is the final expression of the Buckingham expansion in the traceless form [3–5], in which all the multipoles and multipole–multipole polarizabilities are traceless. The transformation from the traced multipoles to the traceless multipoles are given by equations (22a)–(22c). We next derive the transformation from the traced multipole–multipole polarizabilities in equations (6) and (8) to the traceless counterparts,
using the traceless multipoles and the auxiliary traced electric field gradients. Using equation (27), we have:

\[
A_{\gamma,\alpha,\beta} = -3 \frac{\partial^2 U}{\partial F_{\alpha,\beta} \partial E_{\gamma}} = \frac{\partial \Theta_{\alpha,\beta}}{\partial E_{\gamma}} = 3 \frac{\partial \Theta_{\alpha,\beta}}{\partial F_{\gamma}} = 3 \frac{\partial \Theta_{\alpha,\beta}}{\partial F_{\gamma}} J_{\mu,\nu,\rho,\varsigma,\xi} \\
\]

\[
B_{\delta,\epsilon,\alpha,\beta} = -3 \frac{\partial^2 U}{\partial F_{\alpha,\beta} \partial E_{\delta}} = \frac{\partial \Delta_{\alpha,\beta}}{\partial E_{\delta}} = 1 \left( 3 \frac{\partial Q_{\alpha,\beta}}{\partial E_{\delta}} - 3 \frac{\partial Q_{\mu,\nu}}{\partial E_{\delta}} \delta_{\alpha,\beta} \right) \\
\]

\[
C_{\alpha,\beta,\gamma} = -3 \frac{\partial^2 U}{\partial F_{\alpha,\beta} \partial F_{\gamma}} = \frac{\partial \Theta_{\alpha,\beta,\gamma}}{\partial F_{\delta}} = 1 \left( \frac{3}{2} \frac{\partial Q_{\alpha,\beta}}{\partial E_{\delta}} - \frac{\partial Q_{\mu,\nu}}{\partial E_{\delta}} \delta_{\alpha,\beta} \right) f_{\lambda,\gamma} \\
= \frac{1}{6} \left( 9 c_{\alpha,\beta,\gamma} - 3 c_{\alpha,\beta,\mu,\nu} \delta_{\mu,\nu} - 3 c_{\mu,\nu,\gamma} \delta_{\alpha,\beta} \right) + c_{\mu,\nu,\rho} \delta_{\alpha,\beta} \delta_{\rho} \\
\]

\[
D_{\delta,\alpha,\gamma} = -15 \frac{\partial^2 U}{\partial F_{\alpha,\gamma} \partial E_{\delta}} = \frac{\partial O_{\alpha,\gamma}}{\partial E_{\delta}} = 1 \left( 15 d_{\alpha,\gamma} - 3 (d_{\alpha,\mu,\nu} \delta_{\mu,\nu} + d_{\delta,\mu,\nu} \delta_{\alpha,\gamma}) \right) \\
\]

\[
G_{\delta,\beta,\alpha,\gamma} = -45 \frac{\partial^2 U}{\partial F_{\alpha,\gamma} \partial F_{\delta}} = \frac{3 \partial O_{\alpha,\gamma}}{\partial F_{\delta}} = 3 \frac{\partial O_{\alpha,\gamma}}{\partial F_{\delta}} J_{\mu,\nu,\rho,\varsigma,\xi} \\
= \left( \frac{1}{4} \left[ 15 g_{\delta,\beta,\alpha,\gamma} - 3 (g_{\delta,\alpha,\mu,\nu} \delta_{\mu,\nu} + g_{\delta,\beta,\mu,\nu} \delta_{\beta,\alpha} \right) \\
+ g_{\delta,\beta,\mu,\nu} \delta_{\gamma} \right] \delta_{\alpha,\gamma} \right) + \left( \frac{1}{3} \delta_{\beta,\gamma} \delta_{\alpha,\nu} \right) \\
\]

\[
= \frac{1}{4} \left[ 15 g_{\delta,\beta,\alpha,\gamma} - 5 g_{\delta,\beta,\mu,\nu} \delta_{\beta,\gamma} + 3 \left( g_{\delta,\alpha,\mu,\nu} \delta_{\mu,\nu} + g_{\delta,\beta,\mu,\nu} \delta_{\beta,\alpha} \right) \right. \\
+ g_{\delta,\beta,\mu,\nu} \delta_{\gamma} \delta_{\beta,\gamma} + g_{\delta,\beta,\mu,\nu} \delta_{\beta,\alpha} \delta_{\gamma} \\
+ g_{\delta,\beta,\mu,\nu} \delta_{\gamma} \delta_{\beta,\gamma} \right) \\
\]

in which the chain rule is used in order to get the traceless multipole–multipole polarizabilities, with the aid of equations (21a)–(21b). Note that some of the transformations in equation (28), for example, equation (28e), have also been given by Applequist [13] using a different approach. It can be verified using equation (28) by the following traceless identities:

\[
A_{\gamma,\alpha,\beta} = 0 \quad (29a) \\
B_{\delta,\gamma,\alpha,\beta} = 0 \quad (29b) \\
C_{\alpha,\beta,\gamma} = C_{\alpha,\beta,\gamma} = 0 \quad (29c) \\
C^{(2)}_{\gamma,\alpha,\beta,\delta,\eta} = C^{(2)}_{\gamma,\alpha,\beta,\delta,\eta} = 0 \quad (29d) \\
D_{\delta,\alpha,\gamma} = D_{\delta,\alpha,\beta} = D_{\delta,\alpha,\beta} = 0 \quad (29e) \\
G_{\delta,\beta,\alpha,\gamma} = G_{\delta,\beta,\alpha,\beta} = G_{\delta,\beta,\alpha,\beta} = G_{\delta,\alpha,\beta} = 0 \quad (29f) \\
P_{\alpha,\gamma,\delta,\eta} = P_{\alpha,\gamma,\delta,\eta} = P_{\alpha,\gamma,\delta,\eta} = P_{\alpha,\gamma,\delta,\eta} = 0 \quad (29g) \\
\]

In obtaining the above identities, using the first identity \( D_{\delta,\alpha,\gamma} \) in equation (29e) as an example, we have from equation (28e):

\[
D_{\delta,\alpha,\gamma} = \frac{1}{6} \left[ 15 d_{\delta,\alpha,\gamma} - 3 (d_{\delta,\gamma,\mu,\nu} \delta_{\gamma,\mu,\nu} + d_{\delta,\gamma,\mu,\nu} \delta_{\gamma,\nu,\mu}) \right. \\
+ d_{\delta,\gamma,\mu,\nu} \delta_{\mu,\nu} \right] \\
= 0 \quad (28f) \\
\]

in which we use the fact that the repeated sub-index \( \alpha \) is dummy, so that \( \delta_{\alpha,\gamma} = 3 \) and \( \alpha \) can be replaced by another dummy variable \( \mu \), i.e. \( D_{\delta,\alpha,\gamma} = D_{\delta,\gamma,\mu} \); and \( D_{\delta,\gamma,\mu} = D_{\delta,\gamma,\mu} \) since the multipole–multipole polarizabilities are invariant upon the permutation of the sub-indices in the same group. Similar arguments apply on the identities in equations (29e)–(29g). From the above discussions, the traceless feature of the multipole–multipole polarizabilities in equation (28) is the consequence of the traceless electric field gradients, attributed to the Laplace equation.
4. Numerical multipoles and (hyper)polarizabilities with finite field on \textit{ab initio} calculations. A case study on carbon dioxide

Carbon dioxide has attracted much interest, not only for its importance in industry and environmental science, but also for its unique electronic properties as a quadrupole molecule. Buckingham et al. [3, 7] had designed a four-wires condenser to measure the accurate quadrupole of CO$_2$, which laid the foundation for the electric-field-gradient-induced birefringence (EFGIB) experiments [17–19]. The mean and anisotropy dipole polarizability of CO$_2$ could be measured by the depolarization ratio of Rayleigh scattering [20]. Ritchie et al. [21] utilized the Kerr effect to measure the mean second dipole hyperpolarizability, suggested by Buckingham and Pople [6]. On the other hand, higher order multipoles and (hyper)polarizabilities are difficult to directly measure from the experiments nowadays.

Computationally, Maroulis and co-workers have calculated the multipoles and (hyper)polarizabilities of CO$_2$ numerically against high-level \textit{ab initio} calculations with both the charge perturbation method (CPM) [22] and the finite field method (FFM) [10, 23]. In the charge perturbation method, charge is placed at certain distance $R$ from the molecule. Since all orders of electric field and gradients are generated by the charge, according to equation (14), the finite difference is based on the full Buckingham expansion. Moreover, for a polyatom molecule, the point multipole representations are valid only at $R \rightarrow \infty$. Thus, in the actual calculations, the multipoles and (hyper)polarizabilities are often calculated at several different $R$ values, and then extrapolated to $R \rightarrow \infty$ value to refine the result [8]. Such difficulty of the CPM can be overcome by the FFM, in which the electric field or gradient tensors are manipulated directly to generate the desired uniform external field or gradients. In this study, we apply the FFM to calculate the multipoles and (hyper)polarizabilities of CO$_2$ numerically, as detailed in appendix B.

\begin{align}
\alpha_{\alpha\beta} &= \frac{4}{3} \times \frac{U(-E_{\alpha}, E_{\beta}) + U(E_{\alpha}, -E_{\beta}) - U(E_{\alpha}, E_{\beta}) - U(-E_{\alpha}, -E_{\beta})}{4E_{\alpha}E_{\beta}} \\
&= -\frac{1}{3} \times \frac{U(-2E_{\alpha}, 2E_{\beta}) + U(2E_{\alpha}, -2E_{\beta}) - U(2E_{\alpha}, 2E_{\beta}) - U(-2E_{\alpha}, -2E_{\beta})}{16E_{\alpha}E_{\beta}} + O(E_{\alpha}^4), \quad (30)
\end{align}

where $U(E_{\alpha}, E_{\beta})$ denotes the electronic energy calculated at CCSD(T)/daug-cc-pvqz level of theory with finite field of $E_{\alpha} = E_{\beta} = \pm 0.001 \ e/\alpha_0$ applied on the $\alpha$ and $\beta$ directions simultaneously. Equation (30) is derived via Taylor series with solely electric fields applied, as a special case of the Buckingham expansion. Since CO$_2$ is orientated along the principal axes of polarizability with the $z$-axis along the $D_{\infty h}$ symmetric axis, the calculations on $\alpha_{zz}$ and $\alpha_{xx}$ are simpler for the condition $\alpha = \beta$. In this case, $U(-E_{\alpha}, E_{\alpha}) = U_0$ corresponds to the energy without field, and $U(E_{\alpha}, E_{\alpha}) = U(2E_{\alpha})$, etc, so that five \textit{ab initio} calculations are enough, instead of eight \textit{ab initio} calculations, in order to calculate each of $\alpha_{xz}$ and $\alpha_{xy}$ with the FFM.

Similarly, the traced quadrupole and quadrupole–quadrupole polarizability can be calculated with:

\begin{align}
Q_{\alpha\beta} &= \frac{4}{3} \times \frac{U(-E_{\alpha}, -E_{\beta}) - U(E_{\alpha}, E_{\beta})}{2E_{\alpha}E_{\beta}} \\
&= -\frac{1}{3} \times \frac{U(-2E_{\alpha}, -2E_{\beta}) - U(2E_{\alpha}, 2E_{\beta})}{4E_{\alpha}E_{\beta}} + O(E_{\alpha}^4) \quad (31)
\end{align}

in which $U(E_{\alpha}, E_{\beta})$ denotes the electronic energy calculated at CCSD(T)/daug-cc-pvqz level of theory with finite field of $E_{\alpha} = E_{\beta} = \pm 0.001 \ e/\alpha_0$ applied on $\alpha$ and $\beta$ directions simultaneously. The detailed derivation of the above two finite field expressions are given by equations (B5) and (B8) in appendix A. The applied finite field gradient is $E_{\alpha\beta} = 0.0005 \ e/\alpha_0$.

The equilibrium geometry of an electronic ground state CO$_2$, of $D_{\infty h}$ point group, has only one structural degree of freedom, i.e. the C–O bond length $r_{CO}$. In this study, we take $r_{CO} = 2.196 \alpha_0$ (Bohr), as deduced from precise experimental rotational constant of CO$_2$ [24]. The Cartesian coordinate system is set with the $z$-axis along the $D_{\infty h}$ symmetric axis and $x$, $y$, $z$-axes mutually perpendicular, corresponding to the principal axes of both $\alpha_{ZZ}$ and $\Theta_{\alpha\beta}$. In the principal frame, there are two independent components of $\alpha_{ZZ}$, one independent component of $\Theta_{\alpha\beta}$, and three independent components of $C_{\alpha\beta}$, respectively. With the above geometry and coordinate, the \textit{ab initio} calculations, with finite external electric field or gradient applied, were performed at CCSD(T)/daug-cc-pvqz level of theory using the Gaussian16 package [15].

According to equation (6a), with $U$ in equations (12) or (27), the dipole polarizability can be calculated numerically with finite difference, i.e. [25]:

\begin{align}
\alpha_{\alpha\beta} &= \frac{4}{3} \times \frac{U(-E_{\alpha}, E_{\beta}) + U(E_{\alpha}, -E_{\beta}) - U(E_{\alpha}, E_{\beta}) - U(-E_{\alpha}, -E_{\beta})}{4E_{\alpha}E_{\beta}} \\
&= -\frac{1}{3} \times \frac{U(-2E_{\alpha}, 2E_{\beta}) + U(2E_{\alpha}, -2E_{\beta}) - U(2E_{\alpha}, 2E_{\beta}) - U(-2E_{\alpha}, -2E_{\beta})}{16E_{\alpha}E_{\beta}} + O(E_{\alpha}^4), \quad (30)
\end{align}
The traceless quadrupole of CO$_2$ in atomic units ($e \cdot a_0^2$).

|          | CCSD(T)$^a$ | MP4SDQ$^b$ | CCSD(T)$^c$ | CCSD(T)$^d$ | Experiments |
|----------|-------------|-------------|-------------|-------------|-------------|
| $\Theta_{\alpha\beta}$ | $-3.163$ | $-3.239$ | $-3.19$ | $-3.17$ | $-3.0482^e$, $-3.1873^f$, $-3.1806^g$, $-3.1895^h$ |

$^a$ This work.
$^b$ Reference [22].
$^c$ Reference [23].
$^d$ Reference [10].
$^e$ Reference [28].
$^f$ Reference [7].
$^g$ Reference [18].
$^h$ Reference [19].

For CO$_2$ oriented with $z$-axis along the $D_{xh}$ symmetric axis, the traceless condition in equation (25a) implies that $\Theta_{\alpha\beta} = \Theta_{\beta\alpha} = -\Theta_{zz}/2$.

Table 3. The traceless quadrupole–quadrupole polarizability of CO$_2$ in atomic units ($a_0^2$).

|          | CCSD(T)$^a$ | MP4SDQ$^b$ | CCSD(T)$^c$ | CCSD(T)$^d$ |
|----------|-------------|-------------|-------------|-------------|
| $C_{\alpha\alpha}^{zz}$ | $80.878$ | $81.079$ | $80.94$ | $81.14$ |
| $C_{\alpha\beta}^{xx}$ | $34.082$ | $33.021$ | $34.13$ | $33.97$ |
| $C_{\alpha\beta}^{xy}$ | $53.506$ | $54.039$ | $54.81$ | $53.88$ |
| $C_{\alpha\beta}^{zz}$ | $78.158$ | $77.757$ | $79.25$ | $78.39$ |

$^a$ This work.
$^b$ Reference [22].
$^c$ Reference [23].
$^d$ Reference [10].

$e/a_0^2$. Since the symmetric $E_{\alpha\alpha}$ tensor is manipulated in the Gaussian16 package [15] with $E_{\alpha\alpha} = E_{\alpha\beta} = 0.0005 e/a_0^2$ for $\alpha = \beta$ and $E_{\alpha\beta} = 0.001 e/a_0^2$ for $\alpha = \beta$, the actual calculation with the FFM gives $Q_{\alpha\beta} + Q_{\beta\alpha} = 2Q_{\alpha\alpha}$. Thus, the result needs to be further divided by two, as comparing equation (31) with equation (B5). For the same reason, the actual calculation with the FFM gives $c_{\alpha\beta\gamma\delta} + c_{\beta\alpha\delta\gamma} + c_{\alpha\delta\beta\gamma} + c_{\delta\alpha\gamma\beta} = 4c_{\alpha\beta\gamma\delta}$. Thus, the result needs to be further divided by four, as comparing equation (32) with equation (B8). The corresponding traceless quadrupole $\Theta_{\alpha\beta}$ and quadrupole–quadrupole polarizability $C_{\alpha\beta\gamma\delta}$ can be obtained via equations (22a) and (28c), respectively.

Tables 1–3 list the independent components of dipole polarizability, quadrupole and quadrupole–quadrupole polarizability, respectively. Comparisons with high-level ab initio calculations of both the CPM and the FFM, as well as the experimental measurements are also listed for dipole polarizability and quadrupoles in tables 1 and 2. It can be seen that the agreement of current study with previous computational and experimental studies is reasonable. Thus, the general Buckingham expansion in the traced form in equation (B1) is validated. The benefit of equation (B1) is that it can be applied to calculate all the multipoles and (hyper)polarizabilities with accuracy of $OE^2$ for arbitrary order $n$ in a consistent manner with the FFM. Of course, the accuracy of the FFM is also highly dependent on the level of theory and basis set in the ab initio calculations, in order to get an accurate $U(E)$. For further study, we plan to adopt high-level ab initio calculations and extrapolate to the complete basis set limit to get higher accuracy of $U(E)$. 

\[ e/a_0^2 \]
5. Summary

In this study, we derive the Buckingham expansion [3–5] in both traced and traceless forms. Specifically, with explicitly taking the Buckingham convention, aiming on the final form of the Buckingham expansion in its widely accepted form, we derive in section 2 the Buckingham expansion in the traced form using Taylor series. Based on the above derivation, a general Buckingham expansion in the traced form, equation (B1), is proposed. Based on equation (B1), numerical calculations of the multipoles and (hyper)polarizabilities with the finite field method, with accuracy of \( O(E^4) \), in which \( E \) denotes the externally applied finite fields or gradients, is derived. The transformation from the traced multipoles and multipole–multipole polarizabilities to the corresponding traceless counterparts can be performed with an auxiliary traced electric field gradient, as described in section 3. The results of numerical calculations based on the finite field method against high-level \( ab \text{ initio} \) calculations of \( \text{CO}_2 \), as a case study in section 4, are in good agreement with experimental results and previous theoretical calculations. We hope that the method in the current study can be applied to calculations of molecular/ionic multipoles and (hyper)polarizabilities, and further studies are in progress.

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Conflict of interest

The authors declare that they have no conflict of interest.

Appendix A. Comparison with previous works

Buckingham proposed the Buckingham expansion in the traceless form [3–5], but did not provide a complete derivation to the best of our knowledge. McLean and Yoshimine (M&Y) [12], in communications with Buckingham, derived the Buckingham expansion in the traced form with multi-variable Taylor series, and then extended to the traceless form by solving the traceless multipoles using the Laplace equation, and solving the traceless multipole–multipole polarizabilities using the traceless features in equation (29). Our derivation also starts from Taylor series, as presented in section 2. On the other hand, the main difference is that the traceless multipoles and multipole–multipole polarizabilities are derived in section 3 in this work. Thus, equation (29), as the consequence of Laplace equation, is not needed in deriving the traceless multipole–multipole polarizabilities. Since M&Y’s derivation [12] was adopted in many studies in numerical calculations of molecular multipoles and (hyper)polarizabilities [23, 29], we give in this appendix mainly comparison with M&Y’s derivation [12].

Firstly, we need to clarify the convention in M&Y’s derivation [12]. For a charge distribution of \( \rho(r) \) centered at \( O \), represented by point multipoles, the energy \( u \), which is denoted as \( U \) in our study, is a function of electric potential, fields, and gradients, i.e. [12]:

\[
\begin{align*}
    u &= u(\phi, E_x, E_y, E_z, E_{xx}, E_{xy}, E_{xz}, E_{yy}, E_{yz}, E_{zz}, \\
    &\quad E_{xxx}, E_{xxy}, E_{xxz}, E_{xyy}, E_{xyz}, E_{xzz}, \\
    &\quad E_{yyy}, E_{yyz}, E_{yzz}, E_{zzz}, \cdots)
\end{align*}
\]

(A1)

in which the energy \( u_0 \) in zero external field is set to be zero without losing generality. It is notable that only half of the off-diagonal electric field gradient tensor components are included in the above equation. For example, \( E_{xy} \) is included in equation (A1), but \( E_{xx} \) is not included, since field gradient is symmetric and \( E_{xx} = E_{xy} \). Thus, the convention in M&Y’s derivation [12] is that only one of the symmetric electric field gradient components is included in the energy expression. Similarly, by such convention, only one out of the three permutations of the \( vxz \) components is included for \( E_{vxz} \), and one out of the six permutations of the \( vyz \) components is included for \( E_{vyz} \), etc. Specifically, for an \( lth \) rank field gradient tensor, \( E_{\alpha \beta \cdots} \), only one out of the \( d_{\alpha \beta \cdots} \) permutations is included in equation (A1), with:

\[
d_{\alpha \beta \cdots} = \frac{l!}{l_1!l_2!l_3!}.
\]

(A2)

in which \( l_1, l_2, \) and \( l_3 \) are the number of the repeated subscripts \( \{x, y, z\} \), respectively, and \( l = l_1 + l_2 + l_3 \). By such convention, it is understood that only the independent field gradient components, i.e. 6 out of 9 \( E_{\alpha \beta \gamma} \), 10 out of 27 \( E_{\alpha \beta \gamma \delta} \), 15 out of 81 \( E_{\alpha \beta \gamma \delta \epsilon} \), etc, are included in equation (A1). Generally, the number of independent components for an \( lth \) rank tensor is \( \sum_{i=1}^{l+1} i \). Such convention is in distinct difference than the Buckingham convention, in which all the permutations of \( E_{\alpha \beta \cdots} \) are included in the energy expression, as discussed in section 2.

Nevertheless, following the convention of independent field gradient components of M&Y [12], equation (A1) is then expanded via Taylor series in the space of multiple variables, i.e.:

\[
\begin{align*}
    u &= q\phi + \sum_{\alpha} u_{\alpha}^0 + \sum_{\alpha} \sum_{\beta \neq \alpha} u_{\alpha \beta}^0 E_{\beta} + \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \alpha} u_{\alpha \beta \gamma}^0 E_{\beta} E_{\gamma} \\
    &\quad + \frac{1}{2} \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \alpha} \sum_{\delta \neq \alpha} u_{\alpha \beta \gamma \delta}^0 E_{\beta} E_{\gamma} E_{\delta} + \cdots
\end{align*}
\]

(A3)
in which the summation symbol \( \sum \) is explicitly written, because M&Y’s convention imposes the constraints on the range of subscripts for the \( l \)th rank field gradient tensors for \( l \geq 2 \). Apart from that, the exchange of the group of the subscripts, for example, in the constraint summation over \( a_{\gamma\alpha\beta}E_\alpha E_\beta + a_{\beta\gamma\alpha}E_\beta E_\gamma \) in the second line of equation (A3), occurs as a consequence of the Taylor series of multi-variables. It is also notable that due to the inherent exchangeability of the sub-indices \( \gamma \) and \( \delta \) in \( u_{\alpha\beta\gamma\delta}^{(l)} \), the summations over \( u_{\alpha\beta\gamma\delta}^{(l)}E_\alpha E_\beta E_\gamma E_\delta \) are already included in the summations over \( u_{\alpha\beta\gamma\delta}^{(l)}E_\alpha E_\beta \). Also, due to the free permutations of sub-indices \( \gamma \) and \( \delta \) in \( u_{\alpha\beta\gamma\delta}^{(l)} \), the summations over \( u_{\alpha\beta\gamma\delta}^{(l)}E_\alpha E_\beta E_\gamma E_\delta \), have already been included in the summations over \( u_{\alpha\beta\gamma\delta}^{(l)}E_\alpha E_\beta \), and similar for the other two terms involving \( u_{\alpha\beta\gamma\delta}^{(l)} \) and \( u_{\alpha\beta\gamma\delta}^{(l)} \). Thus, all the permutations of the groups of subscripts are allowed, and such convention is also in distinct difference than the Buckingham convention discussed in section 2, and a conversion to the Buckingham convention is needed.

Equation (A3) is the key to understand M&Y’s derivation [12] to solve the multipoles and (hyper)polariabilities. Briefly, the approach taken in M&Y’s derivation [12] is that they firstly released the constraint on the independent electric field gradient variables in equation (A1), and then added a linear combinations of the traceless electric field gradients, i.e. equation (17), into equation (A3). This manipulation does not alter \( u \), but equation (A3) can be transformed to the Buckingham expansion in the traceless form, i.e. equation (27). Next, the traceless features of the multipole–multipole polarizabilities, i.e. equation (29), were invited to solve the coefficients in the linear combination. By equating the coefficients, the individual Cartesian components of the multipoles and (hyper)polariabilities were expressed in the derivatives of \( u \) w.r.t. electric fields or gradients [12].

Here, we take a simple route to get the same results in M&Y’s derivation [12], by taking advantage of some of the derived expressions in section 2 and section 3. Since the multi-variable Taylor series in equation (A3) ought to give the same energy as the Buckingham expansion, by comparing equivalent terms of equation (A3) with the Buckingham expansion in the traceless form in equation (12), and considering the symmetric permutations, we have:

\[
\begin{align*}
u^l &= \frac{\partial u}{\partial E_\alpha} = -\mu_\alpha \quad \text{(A4a)} \\
u^{(l)}_{\alpha\beta} &= \frac{\partial u}{\partial E_{\alpha\beta}} = -\frac{d_{\alpha\beta}}{2} Q_{\alpha\beta} \quad \text{(A4b)} \\
u^{(l)}_{\alpha\beta\delta} &= \frac{\partial u}{\partial E_{\alpha\beta\delta}} = \frac{-d_{\alpha\beta\delta}}{3} O_{\alpha\beta\delta} \quad \text{(A4c)} \\
u^{(l)}_{\alpha\beta\gamma\delta} &= \frac{\partial u}{\partial E_{\alpha\beta\gamma\delta}} = \frac{-d_{\alpha\beta\gamma\delta}}{4} H_{\alpha\beta\gamma\delta} \quad \text{(A4d)} \\
u^{(l)}_{\alpha\beta\gamma\delta} &= \frac{\partial^2 u}{\partial E_\gamma \partial E_\delta} = -\alpha_{\alpha\beta} \quad \text{(A4e)} \\
u^{(l)}_{\alpha\beta\gamma\delta} &= \frac{\partial^2 u}{\partial E_\gamma \partial E_\delta} = -\frac{d_{\alpha\beta}}{2} a_{\gamma\alpha\beta} \quad \text{(A4f)}
\end{align*}
\]

It is notable that equations (A4a), (A4e), (A4i) and (A4k) give the dipole, polarizability, and first and second polarizability, as in equations (5a), (6a), (8a) and (8b). For the others, they give the relations between the derivatives of \( u \) and the traced multipoles and multipole–multipole polarizabilities in equations (5b)–(5d), (6b)–(6d) and (8c). We can next convert the traced multipoles and multipole–multipole polarizabilities to the traceless counterparts using equations (22) and (28), and the results are:

\[
\begin{align*}
\Theta_{\alpha\beta} &= -3 \frac{u_\alpha}{d_{\alpha\beta}} + u_{\mu\nu} \delta_{\alpha\beta} \quad \text{(A5a)} \\
\Omega_{\alpha\beta\gamma} &= -15 \frac{u^{(l)}_{\alpha\beta\gamma}}{d_{\alpha\beta\gamma}} + 3 \left( \frac{u^{(l)}_{\mu\nu\rho\gamma}}{d_{\mu\nu\rho\gamma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\gamma}}{d_{\mu\nu\rho\gamma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\gamma}}{d_{\mu\nu\rho\gamma}} \delta_{\alpha\beta} \right) \quad \text{(A5b)} \\
\Phi_{\alpha\beta\gamma\delta} &= -105 \frac{u^{(l)}_{\alpha\beta\gamma\delta}}{d_{\alpha\beta\gamma\delta}} + 15 \left( \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} \right) \\
&\hspace{2cm} - 3 \left( \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\mu\nu\rho\sigma}}{d_{\mu\nu\rho\sigma}} \delta_{\alpha\beta} \right) \quad \text{(A5c)} \\
A_{\gamma\alpha\beta} &= -3 \frac{u^{(l)}_{\alpha\beta\gamma}}{d_{\alpha\beta\gamma}} + u^{(l)}_{\mu\nu\rho\gamma} \delta_{\alpha\beta} \quad \text{(A5d)} \\
B_{\delta\alpha\beta} &= -3 \frac{u^{(l)}_{\alpha\beta\delta}}{d_{\alpha\beta\delta}} + u^{(l)}_{\mu\nu\rho\delta} \delta_{\alpha\beta} \quad \text{(A5e)} \\
C_{\alpha\beta\gamma\delta} &= -3 \frac{u^{(l)}_{\alpha\beta\gamma\delta}}{d_{\alpha\beta\gamma\delta}} + \frac{u^{(l)}_{\alpha\beta\gamma\delta}}{d_{\alpha\beta\gamma\delta}} \delta_{\alpha\beta} + \frac{u^{(l)}_{\alpha\beta\gamma\delta}}{d_{\alpha\beta\gamma\delta}} \delta_{\alpha\beta} \quad \text{(A5f)}
\end{align*}
\]
\[
\begin{align*}
D_{\alpha\beta\gamma} = -15 \frac{u^{\mu\nu\rho\sigma}_{\alpha\beta\gamma} d_{\rho\lambda}}{d_{\nu\mu}} + 3 \left( \frac{u^{\mu\nu\rho}_{\alpha\beta\gamma} d_{\rho\lambda}}{d_{\nu\mu}} + \frac{u^{\mu\nu\rho}_{\alpha\beta\gamma} d_{\rho\lambda}}{d_{\nu\mu}} \right) \\
+ \frac{u^{\mu\nu\rho}_{\alpha\beta\gamma} d_{\rho\lambda}}{d_{\nu\mu}} \delta_{\alpha\beta}, 
\end{align*}
\]

in which \(d_{\rho\lambda}\) is the permutation of the subscripts \(\alpha\beta\). Note that \(d_{\rho\lambda} = d_{\lambda\rho} = d_{\beta\alpha} = d_{\alpha\beta} = 1\), and similar for the last expressions of equations (A5a)–(A5f). Equation (A5) gives exactly the same traceless multipoles and multipole–multipole polarizabilities as in equation (20) of M&Y’s derivation [12], as can be easily checked. Moreover, equation (A5) is equivalent to equations (22) and (28), which give the multipoles and multipole–multipole polarizabilities in the Buckingham expansion in the traceless form, equation (27), and the permutation factor \(d_{\rho\lambda}\) in equation (A5) is given by equation (A2), in which only one of the symmetry \(d_{\rho\lambda}\) electric field gradient components is included. Of course, since equation (27) includes all the symmetric \(E_{\alpha\beta\gamma}\), the division of \(d_{\rho\lambda}\) is unavoidable for the conversion between equations (A3) and (12).

Finally, we note that some of the gaps in M&Y’s derivation [12] were filled by Applequist, who also adopted multivariable Taylor series with all the electric field and gradient components included. The resultant expression is similar to equation (A3), but with all the Greek subscripts freely varying on \((x, y, z)\). Thus, Applequist’s convention, with free permutations of subscripts and free exchanges of groups of subscripts, is also different from the Buckingham convention, and a conversion is needed. On the other hand, in the derivation we provide in section 2 in this study, the convention is explicitly designed at very beginning. Thus, the derivation is naturally driven to the final form of the Buckingham expansion in the traceless form in equation (12), and no conversions are needed.

Appendix B. Finite field method based on the Buckingham expansion

Based on the discussions in section 2, we propose the following general expression of the Buckingham expansion in the traceless form,

\[
U = q\varphi - \sum_{n_2=0}^{N_2} \cdots \sum_{n_1=0}^{N_1} \sum_{n_2-n_1=0}^{N_2-n_1} c_{\alpha\beta\gamma} P_{\alpha\beta\gamma} E_{\alpha\beta\gamma},
\]

in which \(P_{\alpha\beta\gamma} \cdots \) denotes either multipole or (hyper)polarizability in the traceless form, with \(P_1 = P_{1100\cdots} = \mu\), \(P_0 = P_{000\cdots} = Q_{\alpha\beta}, P_{11} = P_{1100\cdots} = a_{\alpha\beta\gamma}, P_{20} = P_{020\cdots} = c_{\alpha\beta\gamma}, \) etc., and \(P_0 = P_{000\cdots} = -U_0\) as definition. It is understood that the exchange of the sub-indices, i.e. \(P_{\alpha\beta\gamma} \cdots \) is not allowed. For example, for \(P_{11}\) with \(n_1 = 1,\) and \(n_2 = 1,\) so that \(P_{11} = a_{\alpha\beta\gamma}\) is allowed, but \(P_{\alpha\beta\gamma} = a_{\alpha\beta\gamma}\) is not allowed. On the other hand, the permutations of the Greek subscripts in the same place of \(P_{\alpha\beta\gamma}\) is allowed. For example, for \(P_{02}\), both \(c_{\alpha\beta\gamma}\) and \(c_{\beta\alpha\gamma}\) are allowed because the Greek subscripts in the same place of \(P_{\alpha\beta\gamma}\) is allowed. For example, for \(P_{02}\), both \(c_{\alpha\beta\gamma}\) and \(c_{\beta\alpha\gamma}\) are allowed. Such convention is of course consistent with the Buckingham convention, as discussed in section 2. In equation (B1):

\[
c_{\alpha\beta\gamma} = \frac{1}{m!} \frac{1}{2^{n_2}} \frac{1}{3^{n_1}} \cdots, \quad E_{\alpha\beta\gamma} = E_{\alpha\beta\gamma}^0, E_{\alpha\beta\gamma}^0, \cdots
\]

where \(E_{\alpha\beta\gamma}^0\) denotes \(n\)th order electric field Cartesians tensor, with \(l\) Greek subscripts, so that \(E_1 = E_{\alpha\beta}, E_2 = E_{\alpha\beta\gamma}, E_3 = E_{\alpha\beta\gamma\delta}, \) etc. and \(E_0 = 1,\) etc.

Though equation (B1) can be expanded to \(N_\alpha\beta\gamma\) for practical usage only a small portion is enough. For example, let \(N_1 = 2, N_2 = 2,\) and \(N_0 = 0\) for \(l > 2,\) we have the truncated version of equation (B1), i.e.:

\[
U = q\varphi - \sum_{n_2=0}^{N_2} \sum_{n_1=0}^{N_1} c_{\alpha\beta\gamma} P_{\alpha\beta\gamma} E_{\alpha\beta\gamma}
\]

which is comparable to equation (12), with an additional term \(P_{22} = c_{\alpha\beta\gamma} c_{\alpha\beta\gamma}\) called dipole–dipole–quadrupole–quadrupole polarization. Note that the Einstein summation convention is applied on the repeated Greek subscripts in the above expression. For another example, when only the specific electric field \(E_{\alpha\beta}\), i.e. \(\pm E_{\alpha\beta}\), is applied, the resultant Buckingham expansion is reduced to Taylor series of electric field, from which the finite difference expression of dipole polarization \(a_{\alpha\beta}\) can be derived [25], as shown in equation (30) in section 4.

We next derive the finite field expression of the traceless quadrupole \(Q_{\alpha\beta}\) using equation (B1). When only the specific electric field gradient of \(E_{\alpha\beta}\), i.e. \(\pm E_{\alpha\beta}\) is applied, only the corresponding \(P_{\alpha\beta\gamma}\) responses to the power of \(E_{\alpha\beta}\) so that equation (B1) can be simplified to include the contribution solely from \(\pm E_{\alpha\beta}\) i.e.:

\[
U(\pm E_{\alpha\beta}) = - \sum_{n_2=0}^{N_2} c_{\alpha\beta\gamma} P_{\alpha\beta\gamma} E_{\alpha\beta}
\]

where \(P_{\alpha\beta\gamma}\) is quadrupole–quadrupole–quadrupole polarization, and \(P_{\alpha\beta\gamma}\) is quadrupole–quadrupole–quadrupole polarization, respectively. Note that the Einstein summation convention is not applied to equation (B3) because the Cartesian component \(\alpha\beta\) is not dummy as it appears
on the LHS of the expression. From equation (B3), \( Q_{\alpha \beta} \) can be obtained by applying two side finite difference against \( E_{\alpha \beta} \), i.e.:

\[
\frac{U(-E_{\alpha \beta}) - U(E_{\alpha \beta})}{2E_{\alpha \beta}} = Q_{\alpha \beta} + \frac{1}{4} P_{\alpha \beta,\alpha \beta,\alpha \beta} E_{\alpha \beta}^2 + O(E_{\alpha \beta}^4), \tag{B4a}
\]

which gives \( Q_{\alpha \beta} \) with accuracy up to \( O(E_{\alpha \beta}^2) \). Doubling the electric field gradient, i.e. \( \pm 2E_{\alpha \beta} \), we have:

\[
\frac{U(-2E_{\alpha \beta}) - U(2E_{\alpha \beta})}{2E_{\alpha \beta}} = Q_{\alpha \beta} + P_{\alpha \beta,\alpha \beta,\alpha \beta} E_{\alpha \beta}^2 + O(E_{\alpha \beta}^4). \tag{B4b}
\]

Combining equations (B4a) and (B4b) to eliminate the \( P_{\alpha \beta,\alpha \beta,\alpha \beta} E_{\alpha \beta}^2 \) term, we have:

\[
Q_{\alpha \beta} = \frac{4}{3} \times \frac{U(-2E_{\alpha \beta}) - U(2E_{\alpha \beta})}{2E_{\alpha \beta}} - \frac{1}{3} \times \frac{U(-2E_{\alpha \beta}) - U(2E_{\alpha \beta})}{2E_{\alpha \beta}} + O(E_{\alpha \beta}^2). \tag{B5}
\]

The above expression is four-side finite difference against \( E_{\alpha \beta} \) with accuracy up to \( O(E_{\alpha \beta}^2) \), and is adopted in section 4 to calculate the traced quadrupole numerically.

Similarly, the quadrupole–quadrupole polarizability \( c_{\alpha \beta,\gamma \delta} \) can be obtained by applying two specific electric field gradients, \( \pm E_{\gamma \delta} \), simultaneously, and using equation (B1):

\[
U(\pm E_{\alpha \beta}, \pm E_{\gamma \delta}) = -\sum_{n_2=0} c_{0_{n_2}} P_{\alpha \beta,0_{n_2}} E_{\gamma \delta} \quad \text{or} \quad U(\pm E_{\alpha \beta}, -E_{\gamma \delta}) = -\sum_{n_2=0} c_{0_{n_2}} P_{\alpha \beta,0_{n_2}} E_{\gamma \delta}
\]

\[
U(\pm E_{\alpha \beta}, E_{\gamma \delta}) = -\sum_{n_2=0} c_{0_{n_2}} P_{\alpha \beta,0_{n_2}} E_{\gamma \delta} = U_0 + \frac{1}{2} Q_{\alpha \beta} E_{\gamma \delta} + \frac{1}{2} Q_{\gamma \delta} E_{\gamma \delta}
\]

\[
-\frac{1}{4} c_{\alpha \beta,\alpha \beta,\gamma \delta} E_{\gamma \delta}^2 + \frac{1}{8} c_{\alpha \beta,\alpha \beta,\gamma \delta} E_{\gamma \delta}^3 + \frac{1}{16} P_{\alpha \beta,\alpha \beta,\gamma \delta,\gamma \delta} E_{\gamma \delta}^4 + O(E_{\gamma \delta}^4), \tag{B6b}
\]

in which the coefficients in the denominator are determined according to equation (B2), while the coefficients in the numerator are determined according to permutation of the groups of the subscripts, which are inherently exchangeable, as discussed in section 2. From equation (B6), \( c_{\alpha \beta,\gamma \delta} \) can be obtained by four-side finite difference against \( E_{\alpha \beta} \) and \( E_{\gamma \delta} \), i.e.:

\[
\frac{U(-E_{\alpha \beta}, E_{\gamma \delta}) + U(E_{\alpha \beta}, -E_{\gamma \delta}) - U(E_{\alpha \beta}, E_{\gamma \delta}) - U(-E_{\alpha \beta}, -E_{\gamma \delta})}{2E_{\alpha \beta} E_{\gamma \delta}} = \frac{c_{\alpha \beta,\gamma \delta} + \frac{1}{16} P_{\alpha \beta,\gamma \delta,\alpha \beta,\gamma \delta} E_{\gamma \delta}^4 + O(E_{\gamma \delta}^4), \tag{B7a}
\]

which gives \( c_{\alpha \beta,\gamma \delta} \) with accuracy up to \( O(E_{\gamma \delta}^2) \). Doubling the electric field gradient, i.e. \( \pm 2E_{\gamma \delta} \), we have:

\[
\frac{U(-2E_{\alpha \beta}, 2E_{\gamma \delta}) + U(2E_{\alpha \beta}, -2E_{\gamma \delta}) - U(2E_{\alpha \beta}, 2E_{\gamma \delta}) - U(-2E_{\alpha \beta}, -2E_{\gamma \delta})}{8E_{\alpha \beta} E_{\gamma \delta}} = \frac{c_{\alpha \beta,\gamma \delta} + \frac{1}{16} P_{\alpha \beta,\gamma \delta,\alpha \beta,\gamma \delta} E_{\gamma \delta}^4 + O(E_{\gamma \delta}^4), \tag{B7b}
\]

Combining equations (B7a) and (B7b) to eliminate the \( E_{\gamma \delta}^2 \) terms, we have:
The general formula of the electric field gradients is \[ E_M = E_{\alpha\beta\cdots\alpha_M} \]

\[
E_M = e R^{-(2M+1)} \sum_{L=0}^{[\frac{M}{2}]} (-1)^L [2(M-L)-1]!! R^{2L} (R^{M-2L} \delta_{\alpha L})_{\alpha_1 \cdots \alpha_{2L}} \times \delta_{\alpha_{2L+1} \cdots \alpha_M}.
\]

\[ E_M = E_{\nu_1 \nu_2 \cdots \nu_M} = \sum_{\nu_1 \nu_2 \cdots \nu_M} \delta_{\nu_1 \nu_2} \delta_{\nu_3 \nu_4} \cdots \delta_{\nu_{2L-1} \nu_{2L}} \delta_{\nu_{2L+1} \cdots \nu_M}.
\]

In which the sum is over all the different permutations of the subscripts \( \alpha_1, \alpha_2, \ldots, \alpha_M \), including \( N_{\mu \nu L} = M^L / [2^L L! (M - 2L)!] \) terms.

Based on equations (C1) and (C2), the general formula of equations (21a)–(21c) is given as:

\[ J_{E_\alpha \delta_{\beta \gamma}} = J_{\alpha \beta \gamma} = \frac{\partial E_{\alpha \beta \gamma}}{\partial F_{\delta \beta \gamma}} \]

\[ = \sum_{L=0}^{[\frac{M}{2}]} (-1)^L \frac{[2(M-L)-1]!!}{(2M-1)!!} \delta_{\alpha L} \delta_{\beta_{2L+1}} \delta_{\gamma_{2L+2}} \delta_{\alpha_{2L+3} \cdots \alpha_M} \delta_{\beta_{2L+3} \cdots \beta_M} \delta_{\gamma_{2L+4} \cdots \gamma_M}.
\]

And

\[
\Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \sum_{\nu_1 \nu_2 \cdots \nu_M} \delta_{\nu_1 \nu_2} \delta_{\nu_3 \nu_4} \cdots \delta_{\nu_{2L-1} \nu_{2L}} \delta_{\nu_{2L+1} \cdots \nu_M}.
\]

\[ \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M} = \Xi_{\alpha_1 \alpha_2 \cdots \alpha_M}.
\]

in which \( M \) stands for the rank of the traceless electric field gradients \( E_M = E_{\alpha_1 \alpha_2 \cdots \alpha_M} \), \( F = F_M = F_{\alpha_1 \alpha_2 \cdots \alpha_M} \) denotes the corresponding auxiliary traceless electric field gradients, \([M/2]\) represents the largest integer not exceeding \( M/2 \). And in equation (C1):

\[
\frac{4}{3} \times \frac{U(-E_{\alpha\beta}, -E_{\phi\delta}) + U(E_{\alpha\beta}, -E_{\phi\delta}) - U(E_{\alpha\beta}, E_{\phi\delta})}{2E_{\alpha\beta}E_{\phi\delta}}
\]

\[ - \frac{1}{3} \times \frac{U(-2E_{\alpha\beta}, 2E_{\phi\delta}) + U(2E_{\alpha\beta}, -2E_{\phi\delta}) - U(2E_{\alpha\beta}, 2E_{\phi\delta})}{8E_{\alpha\beta}E_{\phi\delta}}
\]

\[ + O(E^2) \]
- $U_0$ as definition. In equation (C5), the operator $\mathcal{J}_{n_1,n_2,\ldots}$ is:

$$
\mathcal{J}_{n_1,n_2,\ldots} = \prod_M \frac{f_M}{M!} (J_{E_{\mu},F_{\nu}})^{n_M}
$$

in which just one corresponding $f_M$ factor in the equation (23) is needed in the operator when $n_M \neq 0$, while $J_{E_{\mu},F_{\nu}}$ need to be carried out $n_M$ times to satisfy the traceless conditions.

Based on the discussions in section 3 and equations (C1)-(C6), we propose the following general expression of the Buckingham expansion in the traceless form:

$$
U = q\varphi - \sum_{n_0=0}^{N_x} \cdots \sum_{n_1=0}^{N_x} \sum_{n_2=0}^{N_x} f_{n_0,n_1,\ldots} c_{n_0,n_1,\ldots} E_{n_0,n_1,\ldots},
$$

(C7)

in which $f_{n_0,n_1,\ldots}$ and $E_{n_0,n_1,\ldots}$ have been defined in equation (B2). And in equation (C7):

$$
f_{n_0,n_1,\ldots} = \frac{1}{M!} \frac{M!}{(2M - 1)!!} f_M
$$

(C8)

where $f_{n_0,n_1,\ldots}$ is the conversion coefficient from traced to traceless multipole or multipole–multipole polarizability tensor, defining that when $n_2 = n_3 = \ldots = 0$, $f_{0,0,\ldots} = 1$.

It is understood that in equation (C7), the exchange of the sub-indices, i.e. $\Xi_{n_0,n_1,\ldots}$ is not allowed. For example, for $\Xi_{11}$ with $n_1 = 1$, and $n_2 = 1$, so that $\Xi_{n_0,n_1,\ldots}$ is not allowed. On the other hand, the permutations of the Greek subscripts in the same plane are allowed. For example, for $\Xi_{02}$, both $C_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta\delta\gamma}$ are allowed because the groups of the Greek subscripts are inherently exchangeable, as discussed in the text. Also, the permutation of subscripts in the same group is allowed. For example, $A_{\gamma\alpha\beta} = A_{\alpha\beta\gamma}$ are allowed. Such convention is consistent with the Buckingham expansion in the traceless form. It is noted that the equation (C8) means that when $n_M \neq 0$, just one corresponding $1/f_M$ factor is needed in the transform, as shown in equations (26a)–(26c). For example, when $n_1 = 0$, $n_2 = 2$, the corresponding energy term transform in equation (26a) from traced to traceless expression is

$$
- \frac{1}{2} c_{\alpha\beta\gamma\delta} E_{\alpha\beta} E_{\gamma\delta} = - \frac{1}{2} c_{\alpha\delta\beta\gamma} E_{\alpha\delta} E_{\beta\gamma} = - \frac{1}{2} c_{\alpha\beta\delta\gamma} E_{\gamma\delta} E_{\alpha\beta},
$$
in which $f_2$ appears just once.

Though equation (C7) can be expanded to $N_{\infty}$, for practice only a small portion is enough. For example, let $N_1 = 2$, $N_2 = 2$, and $N_l = 0$ for $l > 2$, we have the truncated version of equation (C7), i.e.:

$$
U = q\varphi - \sum_{n_0=0}^{2} \cdots \sum_{n_2=0}^{2} f_{n_0,n_2} c_{n_0,n_2} E_{n_0,n_2}
$$

(C9)

in which $U$ is the total electrostatic energy, $E^{(k)}$ represents electric field or gradients of rank $k$, which is the same as our traceless definition, i.e. equation (C1) and when $t = 1$, $p^{(k)}$ is the trace multipole with $p^{(1)} = \mu$, $p^{(2)} = 1/2Q$, $p^{(3)} = 1/6O$, $p^{(4)} = 1/24H$, ... Applequist gave his energy expansion as:

$$
U = q\varphi - \sum_{i=1}^{\infty} \frac{1}{i!} \sum_{k_1, k_2, \ldots, k_i} \frac{\partial^i U}{\partial E^{(k_1)} \partial E^{(k_2)} \cdots \partial E^{(k_i)}} p^{(k_1)} \cdots p^{(k_i)},
$$

(C10)

in which $k_1, k_2, \ldots, k_i$ could traverse from 1 to $\infty$. The equation (C10) is just the multi-variable Taylor expansion where the variables are the electric field and gradients $E^{(k)}$.

The convention adopted by Applequist in equation (C10) is that the permutations of groups $k_1, k_2, \ldots, k_i$ are allowed, which is different from the Buckingham convention, and the permutations of subscripts inside the group are also permitted which is the same as the Buckingham convention. For example, there exists both $p^{(2)}$ and $p^{(2)}$ terms in the equation (C10), while there just exists $a_{\alpha\beta\gamma\delta}$, not $a_{\gamma\delta\alpha\beta}$ in the equation (B1). It should be noted that the energy in equations (B1) and (C10) are equal. By comparing equations (B1) and (C10), we could find the relationships between Applequist’s and our traced definition, i.e.:

$$
p^{(k_1,k_2,\ldots,k_i)} = \prod_M \frac{n_M!}{M!} f_M^m P_{n_0,n_1,\ldots},
$$

(C11)
in which $P_{n_1n_2\cdots}$ is the traceless multipole or (hyper)polarizability defined in the equation (B1) and $n_1 + n_2 + n_3 + \cdots = t$. Then, Applequist defined the general traceless multipole and (hyper)polarizabilities as:

$$
\xi^{(k_1k_2\cdots k_t)} = T_{k_1} T_{k_2} \cdots T_{k_t} p^{(k_1k_2\cdots k_t)},
$$

(C12)

in which $T_{k_i} = (2k_i - 1)! J_{k_i} J_{k_i}$ and the operator $T_{k_i}$ just acts on those indices of the corresponding rank $k_i$ of $p^{(k_1k_2\cdots k_t)}$.

When $t = 1$, $\xi^{(k)}$ is the traceless multipole with $\xi^{(1)} = \mu$, $\xi^{(2)} = \Theta$, $\xi^{(3)} = \Omega$, $\xi^{(4)} = \Phi$, \cdots. With the help of equations (C5), (C6), (C11) and (C12), the relationship between Applequist’s and Buckingham’s traceless multipoles or (hyper)polarizabilities is:

$$
\xi^{(k_1k_2\cdots k_t)} = \frac{[M]^g_{m_1m_2\cdots m_t} (f_{m_1} f_{m_2} \cdots f_{m_t})^{u-1} \Xi_{n_{1}n_{2}\cdots n_{t}}}{\Xi_{n_{1}n_{2}\cdots n_{t}}}.
$$

(C13)

in which $\Xi_{n_{1}n_{2}\cdots n_{t}}$ is the traceless multipole or (hyper)polarizability defined in the equation (C5) and $n_1 + n_2 + n_3 + \cdots = t$.

**References**

[1] Buckingham A D, Fowler P W and Hutson J M 1988 Theoretical studies of van der Waals molecules and intermolecular forces Chem. Rev. 88 963–88
[2] Stone A J 2013 *The Theory of Intermolecular Forces* (Oxford: Oxford University Press)
[3] Buckingham A D 1959 Direct method of measuring molecular quadrupole moments J. Chem. Phys. 30 1580–5
[4] Buckingham A D 1959 Molecular quadrupole moments Quart. Rev. Chem. Soc. 13 183–214
[5] Buckingham A D 1967 Permanent and induced molecular moments and long-range intermolecular forces Adv. Chem. Phys. 12 107–42
[6] Buckingham A D and Pople J A 1955 Theoretical studies of the Kerr effect: I. Deviations from a linear polarization law Proc. Phys. Soc. A 68 905–9
[7] Buckingham A D and Disch R L 1963 The quadrupole moment of the carbon dioxide molecule Proc. R. Soc. A 273 275–89
[8] Bishop D M and Pipin J 1987 Field and field-gradient polarizabilities of $H_2O$ Theor. Chim. Acta 71 247–53
[9] Maroulis G 1998 Hyperpolarizability of $H_2O$ revisited: accurate estimate of the basis set limit and the size of electron correlation effects Chem. Phys. Lett. 289 403–11
[10] Haskopoulos A and Maroulis G 2006 Dipole and quadrupole (hyper) polarizability for the asymmetric stretching of carbon dioxide: improved agreement between theory and experiment Chem. Phys. Lett. 417 235–40
[11] Elking D M, Perera L, Duke R, Darden T and Pedersen L G 2011 A finite field method for calculating molecular polarizability tensors for arbitrary multipole rank J. Comput. Chem. 32 3283–95
[12] McLean A D and Yoshimine M 1967 Theory of molecular polarizabilities J. Chem. Phys. 47 1927–35
[13] Applequist J 1984 Fundamental relationships in the theory of electric multipole moments and multipole polarizabilities in static fields Chem. Phys. 85 279–90
[14] Thakkar A J and Lupinetti C 2006 Atomic polarizabilities and hyperpolarizabilities: a critical compilation Atoms, Molecules and Clusters in Electric Fields: Theoretical Approaches to the Calculation of Electric Polarizability, ed G Maroulis (London: Imperial College Press)
[15] Frisch M J et al 2016 Gaussian 16, Revision B01. (Wallingford, CT: Gaussian, Inc.)
[16] Rhoderick E H 1947 Definition of nuclear quadrupole moments Nature 160 255–6
[17] Chetty N and Couling V W 2011 Measurement of the electric quadrupole moments of CO$_2$ and OCS Mol. Phys. 109 655–66
[18] Watson J N, Craven I E and Ritchie G L D 1997 Temperature dependence of electric field-gradient induced birefringence in carbon dioxide and carbon disulfide Chem. Phys. Lett. 274 1–6
[19] Graham C, Imrie D A and Raab R E 1998 Measurement of the electric quadrupole moments of CO$_2$, CO, N$_2$, Cl$_2$ and BF$_3$ Mol. Phys. 93 49–56
[20] Balachandran Pillai P C and Couling V W 2019 Dispersion of the Rayleigh light-scattering virial coefficients and polarizability anisotropy of CO$_2$ Mol. Phys. 117 289–97
[21] Gentle I R, Laver D R and Ritchie G L D 1989 Second hyperpolarizability and static polarizability anisotropy of carbon dioxide J. Chem. Phys. 93 3035–8
[22] Maroulis G and Thakkar A J 1990 Polarizabilities and hyperpolarizabilities of carbon dioxide J. Chem. Phys. 93 4164–71
[23] Maroulis G 2003 Electric (hyper) polarizability derivatives for the symmetric stretching of carbon dioxide Chem. Phys. 291 81–95
[24] Gruber G, Rossetti C and Bailly D 1986 The carbon dioxide molecule: a test case for the $r_0$, $r_e$ and $r_m$ structures Mol. Phys. 58 627–36
[25] Kurtz H A, Stewart J J and Dieter K M 1990 Calculation of the nonlinear optical properties of molecules J. Comput. Chem. 11 82–7
[26] Alms G R, Burnham A K and Flygare W H 1975 Measurement of the dispersion in polarizability anisotropies J. Chem. Phys. 63 3321–6
[27] Bogaard M P, Buckingham A D, Pieters R K and White A H 1978 Rayleigh scattering depolarization ratio and molecular polarizability anisotropy for gases J. Chem. Soc. Faraday Trans. 1 74 3008–15
[28] Maroulis G 2004 A note on the electric multipole moments of carbon dioxide Chem. Phys. Lett. 396 66–8
[29] Loboda O, Ingrosso F, Ruiz-López M F, Reis H and Millot C 2016 Dipole and quadrupole polarizabilities of the water molecule as a function of geometry J. Comput. Chem. 37 2125–32
[30] Nénon S, Champagne B and Spassova M I 2014 Assessing long-range corrected functionals with physically-adjusted range-separated parameters for calculating the polarizability and the second hyperpolarizability of polyacetylene and polybutadiene chains Phys. Chem. Chem. Phys. 16 7083–8
[31] Oviedo M B, Ilawe N V and Wong B M 2016 Polarizabilities of $\pi$-conjugated chains revisited: improved results from broken-symmetry range-separated DFT and new CCSD(T) benchmarks J. Chem. Theory Comput. 12 2593–602
[32] Burgos E and Bonadeo H 1981 Electrical multipoles and multipole interactions: compact expressions and a diagrammatic method Mol. Phys. 44 1–15