A Bond Order approach to a process oriented fitting of Potential Energy Surfaces

A. Laganà[*]

Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06100 Perugia, Italy

E-mail: antonio.lagana@unipg.it

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[*]To whom correspondence should be addressed

Abstract

Flexible and easy to reuse potential energy surface formulations play an important role in the cooperative assemblage of simulations of chemical processes based on atomistic approaches. We discuss in this paper the fitting of potential energy surfaces for two and three atoms via a Bond Order approach to the formulation of the interaction terms. As a case study, we consider here diatomic and triatomic Nitrogen systems.

1 Introduction

Kinetics and dynamics properties of molecular systems are usually evaluated by integrating relative motion equation on a suitable Potential Energy Surface (PES). This procedure is most often articulated as follows:

(1) Information on the electronic structure of the involved molecular system (mostly ab initio though not infrequently data from other sources are available) are collected;

(2) Available data are fitted into a suitably accurate PES coded as a routine providing a numerical value of the potential energy for the molecular geometry considered;

(3) The routine is checked and corrected for a proper behaviour in the whole internuclear distance space;

(4) Extended dynamical calculations are performed to calculate the properties of interest.

In our laboratory the above mentioned procedure has been incorporated into GEMS (Grid Empowered Molecular Simulator)[1–3] as part of the activities of the COMPCHEM VO (Virtual Organization)[4] first and of the CMMST (Chemistry Molecular and Materials Science and Technologies) VRC (Virtual Research Community)[5] later. As advocated by the Open Science consultation document (see ref.[6]) VRCs should adopt an Open approach to the process of Investigating → Discovering → Analysing → Writing →Publishing → Outreaching → Assessing Science. In particular, VRCs should engage themselves in developing an Open Science cloud (develop common interfaces, data standards, maintenance, interoperability and sustainability) so as to establish an Open Science Cloud for data, protocols and

methodologies (see http://ec.europa.eu/research/openscience/).

In this respect the CMMST VRC promotes:

- the production of both accurate structural data for existing (and, possibly, new) chemical compounds and ab initio efficiency parameters for elementary (and composite) chemical processes in the field of materials, energy, health, technological processes, etc.

- the free reuse of data produced by the members of the related communities as part of the Open Science model to perform simulations generating innovation at higher level of complexity in the above mentioned fields

- the leveraging on resulting chemical knowledge to teach, train and evaluate people in education and professions.

More specifically, in the recent past the CMMST VRC has specialized GEMS to the systematic study of the homonuclear chemical processes of Nitrogen. Within this effort, several studies have been devoted to the formulation of a full-dimensional PES of $N + N_2$ starting with a LEPS published in ref.[7] Later the LEPS PES was improved to exhibit a double barrier Minimum Energy Path (MEP) using a Largest-Angle Generalized ROtating Bond Order (LAGROBO) methodology based on Bond Order (BO) coordinates[8] to fit a set of available high-level ab initio data.[9,10] Further ab initio calculations were performed later and two new full-dimensional surfaces were published,[11,12] both confirming a double barrier structure for the $N + N_2$ MEP. The investigation was also extended to $N_2 + N_2$ by focusing initially only on the inelastic channel. Accordingly, the PES was initially formulated as a sum of the two N_2 intramolecular interactions and of an intermolecular component (ie that of two separated nitrogen molecules with their internuclear distances close to equilibrium) described in terms of isotropic and anisotropic contributions. For this purpose expansions in spherical harmonics (see for example refs[13–18]) and bond-bond pairwise additive interaction (see ref[19]) were used. The LAGROBO approach was also extended to four nitrogen atom systems.[20] Studies of the interaction components of non reactive processes of $N_2 + N_2$ have been reported in ref.[21,22] In order to include in the study atom exchange and fragmentation

(of one (or both) molecule(s)) processes further ab initio studies were performed for a wide set of molecular geometries.[23–25] and fitted using also a statistically localized, permutationally invariant, local moving least squares interpolating function.[26,27] This feature provides the fitted PES with sufficient flexibility to improve the qualiy of dynamical studies and allow a valid description of high energy processes (including dissociation). Moreover, it makes consistent the formulation of two, three and four body components of the interaction. For this reason it has been also used to the end of carrying out our extended calculations of thermal rate coefficients and detailed state specific collision induced cross sections.[28] This has also motivated our efforts to develop out of it a Bond Order based version.

Acccordingly the paper is organized as follows:

in section 2 global Model Approaches and Local-Mobile Methods to the formulation of potential energy surfaces are discussed,

in section 3 some two body process-driven fitting methods are analyzed,

in section 4 a few body proposal for fitting potentials is discussed,

in section 5 an analysis of the N_2 + N_2 four body case is reported and

in section 6 some conclusions are drawn.

2   Global Model approaches and Local-Mobile Methods for the formulation of potential energy surfaces

The most general procedure for formulating a global PES is based on the weighted Least Squares (LS) method.[29] The LS method expands the PES in terms of the $\mathbf{f}_k(\mathbf{r})$ basis functions depending on the collection of coordinates $\mathbf{r}$ on which it is formulated with c_k being the coefficients of such expansion

$$V(\mathbf{r}) = \mathbf{c}^T \mathbf{f}(\mathbf{r}) = \mathbf{f}^T(\mathbf{r})\mathbf{c} = \sum_{l=1}^{L} c_l f_l(\mathbf{r}). \tag{1}$$

In eq. 1 $\mathbf{c}$ and $\mathbf{f}$ are column vectors, the superscript T denotes as usual "transpose" and L is the number of basis functions. The coordinates and energy values of the data points to be interpolated are $\mathbf{r}(i)$ and $v(i)$, respectively, with $i = 1, 2, .., i_{max}$ and i_{max} being the number of data points.

In a LS fit to the PES one determines the coefficients c_k, by considering the functional weighted squares of the deviations of the fitted potential from the calculated data $\sum_{i=1}^{i_{max}} w_i [V(\mathbf{r}) - v(i)]^2$ in which w_i is the weight associated with the ith point (in fitting *ab initio* points w_i is sometimes chosen to weight more the points located around the minimum energy path of the considered process channels although they are often taken to be unity). By minimizing this functional (that is equivalent to it being stationary with respect to variation in the parameters c_k) one obtains the following "normal" equations:

$$FWF^T\mathbf{c} = FW\mathbf{v}, \tag{2}$$

where W is the diagonal matrix of all the weights w_i

$$W = \mathrm{diag}[w_1, w_2, ..., w_{i_{max}}], \tag{3}$$

and F is the matrix of the values of the basis functions $f(\mathbf{r})$ at $\mathbf{r}(i)$:

$$F = \begin{pmatrix} f_1(\mathbf{r}(1)) & f_1(\mathbf{r}(2)) & ... & f_1(\mathbf{r}(i_{max})) \\ f_2(\mathbf{r}(1)) & f_2(\mathbf{r}(2)) & ... & f_2(\mathbf{r}(i_{max})) \\ ... & ... & ... & ... \\ f_L(\mathbf{r}(1)) & f_L(\mathbf{r}(2)) & ... & f_L(\mathbf{r}(i_{max})) \end{pmatrix}. \tag{4}$$

Functions f_k can be freely chosen. However, a choice typical of spectroscopic studies of stable molecules is a polynomial in all the involved variables (a multinomial) multiplied by an exponential in the dissociating coordinate(s) so as to enforce the correct asymptotic limit. Equations 2 only need to be solved once and the simple linear form of related solutions

allows for very efficient evaluation. Yet, the quality of the fit obtained in this way strongly depends on the choice made for the number and nature of the basis functions and may bear spurious structures in localized regions of the potential. This can be avoided by resorting to extended (a large number of molecular geometries) ab initio calculations so as to dominate the tendency of polynomials in the internuclear distances to diverge at intermediate range before being damped by the related exponentials. This technique has become recently very popular and has fostered the use of local methods. A great advantage of these methods is, in fact, the possibility of improving the fitting (if either further molecular geometries need to be considered or the available fit is insatisfactory) by simply adding more *ab initio* values relative to nearby geometries (though not necessarily located on a uniform grid). Still, however, it is wise to use polynomials in coordinates enforcing the smooth vanishing of the PES at long distance[30,31] (as will be discussed in more detail later) and to leverage as well on the symmetry of the system to simplify the formulation of the PES.[32]

Accordingly, significant efforts have been paid to develop Moving Least Squares (MLS) techniques which mix together global (a linear LS algorithm that is similar to the global one) and a local (basis functions which are only used locally to the geometry of interest) features.[29] Because of this, low order polynomial functions are needed though the coefficients of the basis functions are now functions of geometry, and therefore a heavier computational effort is required for the evaluation of the surface.

In the MLS scheme[33] the value $V(\mathbf{r})$ at point $\mathbf{r}$ is represented again by a linear combination of linearly independent basis functions $f_k(\mathbf{r})(j = 1, ..., n)$:

$$V(\mathbf{r}) = \mathbf{c}^T(\mathbf{r})\mathbf{f}(\mathbf{r}) = \mathbf{f}^T(\mathbf{r})\mathbf{c}^T(\mathbf{r}) = \sum_{l=1}^{L} c_l(\mathbf{r})f_l(\mathbf{r}). \tag{5}$$

Yet in MLS the coefficients $c_1(\mathbf{r}), c_2(\mathbf{r}), ..., c_L(\mathbf{r})$ are allowed to depend on the coordinates $\mathbf{r}$ used to define the PES by using coordinate dependent weight functions.

Being as before the coordinates and energy values to be interpolated $\mathbf{r}(i)$ and $v(i)(i =$

$1, 2, .., i_{max}$) with i_{max} the number of data points, the error functional is given by $\sum_{i=1}^{i_{max}} w_i(\mathbf{r})[V(\mathbf{r})-$ $v(i)]^2$ where now the weights w_j are functions of $\mathbf{r}$). From the condition that the error functional be stationary with respect to variation in the parameters $c_k(\mathbf{r})$, the following generalized normal equations are obtained:

$$FW(\mathbf{r})F^T\mathbf{c}(\mathbf{r}) = FW(\mathbf{r})\mathbf{v} \qquad (6)$$

with the weights w_j, which vary with $\mathbf{r}$, being larger for data points that are close to $\mathbf{r}$ than for points far away. Owing to the fact that the weights depend on position, the expansion coefficients $c_j(\mathbf{r})$ must be obtained from a solution of Eq. (6) for each value of $\mathbf{r}$ where the potential needs to be determined.

To calculate the gradient of the energy at any point (as it would be needed, for example, in a trajectory calculation), take the first derivative of Eq. (5):

$$u_s(\mathbf{r}) = \mathbf{c}_s^T(\mathbf{r})\mathbf{f}(\mathbf{r}) + \mathbf{c}^T(\mathbf{r})\mathbf{f}_s(\mathbf{r}). \qquad (7)$$

Here $c_s(r)$ (the derivative of $c(r)$ with respect to the sth coordinate) is obtained by solving the following equation

$$FW(\mathbf{r})F^T\mathbf{c}_s(\mathbf{r}) = FW_s(\mathbf{r})[\mathbf{v} - F^T\mathbf{c}(\mathbf{r})]. \qquad (8)$$

The interpolated energy and gradient values at any point can be obtained by solving Eqs. (6) and (8) which have dimensions equal to the number of basis functions used. For trajectory calculations, this solution is fairly time consuming for a large number of basis functions. This can be overcome by calling on an IMLS (Interpolant MSL) technique in which equations (6) and (8) (and equivalent expressions for the second derivatives) are used to define gradients and hessians at the positions of the *ab initio* data points, and then the results are used to define a Shepard interpolation in which the potential is represented as a

weighted sum of Taylor expansions about each ab initio point.[29]

3   Process Driven Fitting Methods: a unified view of the two body interactions

Although local mobile fitting methods bear a high degree of flexibility in the choice of coefficients, functional forms and grids of molecular geometry internuclear distance values, they have not yet become of widespread use in actual calculations. In fact, in general, their application is particularly demanding in terms of the number of molecular geometries to be considered for the ab initio calculations of the electronic structure while being poor in terms of the correspondence between the estimated values of the **c** coefficients and physical properties. In order to achieve the objective of both reducing the number of needed ab initio computations and associating a more direct physical meaning to the coefficient values generated by the fitting proedure, we devoted significant efforts to work out possible relationships between the local formulation of the interaction and related processes and observable quantities.

The obvious starting point of our investigation has been the formulation of the potential $V(r)$ of two body processes (typically the elastic atom-atom scattering (weak interactions) and diatomic spectroscopy (strong interactions) like those of the N-N system considered here as a case study) which are defined in one dimension (r the diatomic internuclear distance) once the electronic energy has been adiabatically separated using the Born-Oppenheimer approximation. The first family of functional formulations of the $V(r)$ potential was designed to describe bound systems and processes involving diatomic eigenstates (typically diatomic vibrations for spectroscopic and intramolecular dynamics studies usually associated, as already mentioned, with stronger interactions). At the beginning of spectroscopic studies the potential used to be expressed in terms of powers of r (or better $r - r_e$ with r_e being the equilibrium distance of the diatom) by referring to the Harmonic Oscillator (HO) model

$V^{HO}(r) = k(r - r_e)^2$ and then generalized to the anharmonic case as a polynomial of the fourth order

$$V^{spectr}(r) = \sum_{j=2}^{4} \frac{f_j}{j!}(r - r_e)^j \tag{9}$$

In eq. 9 for N_2 $f_2 = 10^2 22.78$ aJ/nm^2, $f_3 = -177.6110^3$ aJ/nm^3, and $f_4 = 1195.2810^4$ aJ/nm^4 are the harmonic, cubic and quartic force costants of the diatomic oscillator,[34] respectively.

The second type of formulations of the two body $V(r)$ potential, more recent than those of spectroscopy, were designed to describe atom atom collisional (scattering) processes usually associated with weaker interactions. In this case, the two body potential $V(r)$ is most often formulated in terms of inverse powers of r (typically Lennard-Jones 12-6 (LJ) and its variants)

$$V^{scatt}(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6} \tag{10}$$

and refers mainly to long range interactions (its parameters are often formulated also in terms of ε the depth of the associated well).[30,35]

Given the above defined formulations of a weak and a strong interaction component of a two body process channel (subtending the variations occuring in the associated multidimensional electronic structure problem), a popular practice aimed at matching them in a single expression consists in defining a switching function turning the two components either on or off. This approach, however, can easily lead to spurious structures in the intermediate region.

A way of coping with this problem is first the introduction in both formulations of corrections providing additional flexibility useful to facilitate their matching in the intermediate region. This is indeed the case of the strong interaction when multiplying a polynomial of the type given in Eq. 9 by an exponential damping function (EDAP, Exponentially Damped Anharmonic Potential)[36]

$$V^{edap}(r) = \sum_{j=1}^{J} c_j(r - r_e)^j e^{-(r-r_e)} = P(r)e^{-\gamma(r-r_e)}. \tag{11}$$

that results in a smoothly vanishing $V(r)$ mimicking the form of $V^{scatt}(r)$ at large distances (provided that γ is properly chosen). A popular re-formulation in this sense of the strong interaction of Eq. 9 is the Morse potential that reads as:

$$V^{morse}(r) = D_e(e^{-2\gamma(r-r_e)} - 2e^{-\gamma(r-r_e)}) \tag{12}$$

in which γ is equal to the square root of the ratio between the force constant of the diatom and twice its dissociation energy D_e. A reformulation of the weak interaction of Eq. 10 the LJ potential is generalized into an Improved LJ (ILJ)[35] one as follows

$$V^{ILJ}(r) = \varepsilon_o \left[\frac{m}{n(x) - m} \frac{1}{x^{n(x)}} - \frac{n(x)}{n(x) - m} \frac{1}{x^m} \right] \tag{13}$$

where $x = r/r_e$ and $n(x) = \beta + 4x^2$. In this way the increasing deformation of the atomic electronic distributions as the two atoms approach the short range region is accounted for by a modulation of both the repulsive and the long range attractive components of the interaction. In Eq. 13 the value of the parameter β ranges from 6 to 10 (depending on the hardness of the interacting electronic distributions) and could be estimated using the empirical formula

$$\beta = 6 + \frac{5}{s_1 + s_2} \tag{14}$$

where subscripts 1 and 2 identify the colliding partners and s_1 and s_2 stand for the related softness parameters which are related to the cubic root of the polarizability. Moreover, for neutral-neutral systems, ε_o and r_e can be given in terms of the polarizability of the interacting partners. For N_2 the values of the mentioned parameters are: m=6, ε_o=0.00643 eV, r_e=3.583Å. and β=6.6055.

The above mentioned modifications make the transition from the atom-atom (scattering) long range to the diatom (spectroscopy) short range formulation of the interaction smoother (even when using simple switching functions). This becomes of paramount importance par-

ticularly in the regions of the molecular geometries where fewer calculated ab initio values are available. This further advance in matching scattering and spectroscopy biased formulations of the two body PES can be even more profitably exploited to the end of defining a continuity variable enabling the assemblage of a unified simple polynomial expression for $V(r)$. An ideal candidate for this unification is, indeed, the already mentioned Bond Order, BO, coordinate $n = e^{-\gamma(r-r_e)}$ (whose γ parameter is numerically determined to reproduce the diatomic force costants of higher order (see ref.[30])) whose polynomials

$$V^{BO}(r) = D_e \sum_{j=0}^{J} c_j n^j \tag{15}$$

bears interesting properties. In particular, the BO polynomial naturally incorporates the key advantages of the $V^{morse}(r)$ potential that corresponds to its truncation to the second order. Namely: the inverted (with respect to r) Harmonic-like shape confined between $n = 0$ (infinite distance and potential energy equal to the dissociation energy) and $n = e^{\gamma r_e}$ (zero distance and large potential energy) with a minimum at n=1 (equilibrium distance and minimum energy).

This inverted nature of the BO space allows a straightforward extension of the BO polynomial to incorporate also the main features of the long range potential. This can be obtained either through a separate fitting to the long range interaction values of the higher order r^{-j} terms as r increases and to the short and equilibrium range interaction values of the Morse like low order ones up to some multiple of r_e (then connected via a switching function) or through a higher order single BO polynomial global fitting of both the long and short range interactions. Results obtained for the N_2 case are shown in the Table below

Table 1: Coefficients of the N_2 BO potentials formulated using D_e=954.92 kJ/mol and r_e=0.1098 nm. RMSD(BO4)= 4.33 kJ/mol, RMSD(BO6)=2.72 kJ/mol.

PES	c_1	c_2	c_3	c_4	c_5	c_6
BO_4	2.4200	-1.9573	0.6547	-0.1174		
BO_6	2.9833	-3.7743	2.9145	-1.4858	0.4077	-0.0457

Further advantages of using a BO formulation of mobile local potential nature can be obtained by segmenting the BO space in different intervals and optimizing with appropriate criteria related coefficients for each segment while keeping a common functional form (avoiding so far the use of different functions to switch between). This concept, recently developed in ref.[37] by defining the so called Space Reduced (SRBO) version of the BO variables, allows a wise (separate) sampling of the interaction in the BO space in order to balance the number of ab initio points to be calculated in different distance ranges. The SRBO method allows also an appropriate identification of neighbor ab initio points, a better definition of sectors of propagation sectors for the integration of quantum Time Independent scattering equations as well as the singling out of a suitable continuity variable also for electronic state jump processes in two body systems.

4 Process Driven Fitting Methods: three body interactions

After having discussed the use of BO polynomials in one dimension for formulating two body interactions let us turn our attention to their use for three body interactions in which existing bonds can be either heavily deformed or even broken-formed due to the interaction with a third atom. In the past we have already investigated the use of two dimensional BO polynomials for (fixed angle) three body interactions and their variants for different atom diatom arrangements.[31] Our main target was the proper description of the evolution of the interaction channel for reactive bimolecular events (like the fixed collision angle atom B transfer (from BC to AB) reaction A + BC → AB + C and its three dimensional generalization named LAGROBO. The most popular description of the fixed angle $\Phi_B = A\hat{B}C$ A + BC → AB + C reaction channel is given in terms of the related internuclear distances (sometimes also in terms of the relevant Jacobi coordinates) and can be followed in terms of a deformation of a diatomic-like model potential (most often a Morse-like function) starting

with that of the BC reagent and ending up to be that of the AB product. To ensure a smooth switching from one atom-diatom limit to the other, the usual procedure is to introduce the polar coordinates σ_B^r and η_B^r defined as follows[38,39]

$$\sigma_B^r = [(r_{AB}^* - r_{AB})^2 + (r_{BC}^* - r_{BC})^2]^{1/2} \tag{16}$$

$$\eta_B^r = \tan^{-1}\left[\frac{(r_{BC}^* - r_{BC})}{(r_{AB}^* - r_{AB})}\right] \tag{17}$$

with r_{AB} and r_{BC} being the two internuclear coordinates, r_{AB}^* and r_{BC}^* defining the origin of the coordinate system (chosen to have values larger (say about three times) than the corresponding diatomic equilibrium distances in order to be placed in the classically forbidden region separating asymptotically the reactant from the product channel and avoid the loss of flux). Similarly, one can define σ_C^r and η_C^r for the pair of r_{BC} and r_{CA} internuclear coordinates, and σ_A^r and η_A^r for the pair of r_{CA} and r_{AB} internuclear coordinates. The key advantage of these coordinates is the possibility to define a (sometimes piecewise) continuity coordinate for collisions penetrating inside the strong interaction region.

In order to avoid the mentioned critical choice of the origin of the polar coordinate system, one can resort into using the corresponding fixed Φ_I polar formulation of the BO coordinates. For the polar BO coordinates the origin can be safely placed at the common origin of the two involved BO variables as formulated in the so called ROtating BO (ROBO)[40] with no loss of flux. An interesting feature of these coordinates lies in the fact the related angle ϕ_I defined as

$$\phi_I = \tan^{-1}\left[\frac{n_{I-1,I}}{n_{I,I+1}}\right] \tag{18}$$

(where I is any atom of the triatom modulus 3 and ± 1 are the follwing and the preceding one) is a continuity variable connecting the reactant diatom of hannel I to the product one. At the same time the variable ρ defined as:

$$\rho_I = [n_{I-1,I}^2 + n_{I,I+1}^2]^{1/2} \tag{19}$$

spans the different fixed angle elongations of the system whose interaction can be formulated as a polynomial in ρ as follows

$$V_I^{BO}(\Phi_I, \phi_I; \rho_I) = A \sum_{j=0}^{J} c_j \rho_I^j \qquad (20)$$

and coincides with the potential of the separated diatom (either reactant or product) at $\phi_I = 0$ and $\phi_I = \pi/2$. The polynomial given in 20 is able to reproduce single- and multi-minimum structures at intermediate values of ϕ_I allowing the description of distorted triatomic geometries as well as the branching of the reaction entrance channel into different product ones. Accordingly, a simple local model dependence of the ρ polynomials $V_I^{BO}(\Phi_I, \phi_I; \rho_I)$ (parametric in Φ_I and ϕ_I) can be worked out in order to be able to best fit the overall PES and to properly approximate locally its shape in the neighboor regions from a limited (properly weighted) nearby ab initio points while featuring a physically grounded meaning of the parameters. Among the strategies allowed by the LAGROBO treatment there is the one of giving a larger weight to the collinear geometries because they are the ones more accurately determined by several ab initio techniques. Further advantages can be obtained by adopting the SRBO formalism that, by enabling an optimized segmenting of the continuity variable, permits a continuous adaptation to the arrangement channel considered to the exploration of an ad hoc optimized descritpion of the potential channel assciated with the desired process. This approach leads to a generaliation of the so called Many Process Expansion (MPE) MPE (MPE-MEP)[41] in which the local mobile choice of the $\mathbf{c}_s$ fitting coefficients is driven by the localization of the MEP of the different MPEs.

5   Conclusions and future work

The effort of addopting BO formulations for 2 and 3 atom systems is shown in this paper to pay back in terms of producing flexible and smooth potential energy surfaces. Further work is being spent to generalize the BO formulation to four or more atoms by considering

each bond breaking, forming or/and exchanging as an individual process. Particular effort is being spent in collaboration with F. Pirani and his collaborators to tackle the case of the $N_2 + N_2$ for which a symmetric version of the BO four body cooordinates has been already elaborated that can be easily adapted to describe the two diatoms channels as well as the atom triatom one.[20] Related ROBO parameters have been best-fitted both to the spectroscopic and ab initio data of the related diatoms at the asymptotes as well as to the kinetic and ab initio information related to the reaction channel so as to connect smoothly the reactant and product asymptotes through the intermediate structures. Additional effort will be spent to the end of extending the long range interaction to match the short range one at intermediate distances. To this end leverage will be made on the dependence of the molecular electronic polarizability $\alpha(r)$ and of the electric quadrupole moment $Q(r)$ on r.

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