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# Constructing high-accuracy intermolecular potential energy surface with multi-dimension Morse/Long-Range model

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## ABSTRACT

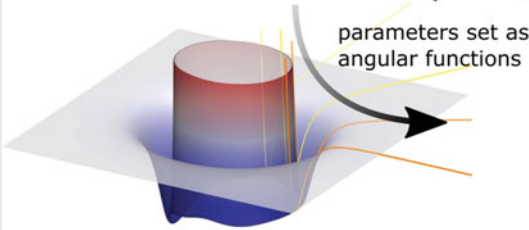
Spectroscopically accurate Potential Energy Surfaces (PESs) are fundamental for explaining and making predictions of the infrared and microwave spectra of van der Waals (vdW) complexes, and the model used for the potential energy function is critically important for providing accurate, robust and portable analytical PESs. The Morse/Long-Range (MLR) model has proved to be one of the most general, flexible and accurate one-dimensional (1D) model potentials, as it has physically meaningful parameters, is flexible, smooth and differentiable everywhere, to all orders and extrapolates sensibly at both long and short ranges. The Multi-Dimensional Morse/Long-Range (mdMLR) potential energy model described herein is based on that 1D MLR model, and has proved to be effective and accurate in the potentiology of various types of vdW complexes. In this paper, we review the current status of development of the mdMLR model and its application to vdW complexes. The future of the mdMLR model is also discussed. This review can serve as a tutorial for the construction of an mdMLR PES.

## ARTICLE HISTORY

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$$V = V_{\text{MLR}}(R) = \mathfrak{D}_e \left\{ 1 - \frac{u_{\text{LR}}(R)}{u_{\text{LR}}(R_e)} e^{-\beta(R) \cdot y_p^{\text{eq}}(R)} \right\}^2 + V_{\text{lim}} - \mathfrak{D}_e$$


$$V = V_{\text{MDMLR}}(R; \Omega) = V_{\text{MLR}}^{\Omega}(R)$$

## 1. Introduction

Non-bonded interactions are one of the most fundamental subjects in physical chemistry, and lie at the core of supramolecular chemistry [1], mechanochemistry [2] and life sciences. Although intramolecular non-bonded interactions such as the ones driving the high-level structure of protein are also very important, intermolecular complexes, or van der Waals (vdW) complexes serve as prototypes for investigating non-bonded interactions. Infrared (IR) and Microwave (MW) spectroscopic studies are perhaps the most direct experimental way to examine this type of interaction, while from the viewpoint of *ab initio* theory, only the smallest vdW complexes may be treated to full spectroscopic accuracy with currently available algorithms and computers.

The Potential Energy Surface (PES) is the most important concept associated with the Born–Oppenheimer approximation [3], and its construction is usually the first step in the theoretical study of spectroscopy and molecular dynamics. For such applications, analytical PESs clearly provide the most compact, portable and straightforward way to summarise the dynamical properties of the nuclei. The potential function model, which is the basis of an analytical PES, is a critical factor determining the quality, reliability and practical utility of a PES.

Numerous intermolecular interaction models have been proposed, and they may be loosely classified into two groups: ‘Mathematical models’ and ‘Physical models’ [4]. On the one hand, the popular Neural Network Potential Energy Surface (NNPES) and its variants pay little attention to the particular nature of the system studied,

and its parameters (in the case of neural networks, let us say ‘weights’) have no clear physical meaning. Although someone may argue that the neurons in the networks can be thought of as being ‘physically meaningful’ [5], people have not been able to decide their meaning before training the network. On the other hand, ‘Physical models’ are based on a clear physical vision on the system, and some of their central parameters are key properties such as well depth(s), bond lengths and multipole moments. Although the super-surfaces can be very complex, parts of the nature of the system can be known without performing calculation from the values of some of the parameters defining such a ‘Physical’ function. Moreover, if they are well designed, the accuracy of such ‘Physical’ models can be increased without adding too many redundant parameters, which means that higher computational efficiency is possible.

The traditional way to describe the interaction inside an atomic or molecular system is to use a force-field in which the intermolecular interaction is represented by the sum of the pairwise interactions between the atoms comprising the two interacting monomers (a site-site potential). The site-site pair potential is then represented using some potential function model that takes account of the charge on each atom. This picture is simple and easy to understand, but it is too coarse for spectroscopic research. For accurate work, it is necessary to treat the interacting molecule as a whole, with the interaction energy being defined as a function of the distance between the two molecules and their relative orientations, while taking account of the molecule’s multipole moments and multipole polarisabilities. Within this framework, the intermolecular potential models are usually explicit functions of the distance between the two monomer centres of mass and the relative orientation angles. Super-spherical harmonic functions are often used to describe the variation with the angles, while the radial part is governed by some analytic function (model), which is usually a variant of some atom-atom interaction potential. Some general models represent this radial behaviour as the sum of a short-range potential plus an asymptotic potential for the long-range region [6–10], as is the case for the exponential Spline-Morse-Morse-Spline-van der Waals form [11,12]. It is important to note that the angular functions and radial functions can be combined in different ways. In particular, the final potential function can be: (a) a sum of products of radial functions with the angular functions, or (b) a radial function whose parameters are expanded in terms of those super-spherical angular functions [12,13].

Direct fitting to spectroscopic data is perhaps the most accurate way to determine an intermolecular PES [14–18]. The problem is that before fitting to optimise the

potential energy function parameters, it is necessary that the spectra be assigned. However, this leads to a kind of paradox, as experimental spectroscopists, even ones who are very experienced and skilled, often must call for theoretical and computational help because the complexity of the spectra they measure is beyond the limit of their intuitive pattern recognition abilities. In contrast, an *ab initio* PES can be constructed without any knowledge of the system itself, and ever more accurate electronic structure methods and ever more powerful computers allow us to generate a PES and make predictions that lie within the accuracy of the spectra, which allows them to be assigned properly [7,19,20].

The main difference between ‘inter-atomic’ and intermolecular interactions is of course the fact that the molecules’ relative alignment, i.e. the orientation angles, can affect the potential. The intermolecular interaction is therefore often represented as a function of the separation distance and the orientations of the relevant molecules. The intramolecular coordinates (bond lengths and angles within the monomers) can also affect the intermolecular interaction. However, because the changes in the intermolecular interaction associated with the intramolecular coordinates are usually small relative to those due to changes in the intermolecular separation and orientations, it is often a reasonable approximation to fix the monomers’ geometry [7]. However, intramolecular coordinates can be the key source of some interesting spectroscopic properties of vdW complexes, such as band origin shifts in the IR spectra [19–22].

An atom-atom interaction, which is a function only of the distance between the two nuclei, is a one-dimensional (1D) problem, while for the intermolecular case, more dimensions are required. The 1D case can be handled very effectively with the Morse/Long-Range (MLR) [23–25] model, which is flexible, accurate and physically meaningful. Based on that 1D MLR model, a Multi-Dimensional Morse/Long-Range (mdMLR) model has been developed to handle atom-molecule and molecule-molecule interactions. Like the original 1D MLR model, the mdMLR model is flexible, robust, accurate, analytically derivable everywhere and physically meaningful.

In this review, the development of the mdMLR model is introduced. In Section 2, the *ab initio* calculation methods used in construction of intermolecular PESs are briefly introduced; In Section 3, the 1D MLR model is briefly introduced; In Section 4, general idea of expand 1D MLR to mdMLR are described and forms of mdMLR model are presented with their applications to real vdW complexes in Section 5; In Section 6, the advantages and shortcomings of the mdMLR model are discussed. This work can serve as a tutorial regarding the construction of a PES using an mdMLR model.

## 2. *Ab initio* calculation

The quality of the input *ab initio* calculation is critical in the construction of a PES. Without sufficiently accurate input data, even the most sophisticated post-processing can be pointless.

Electronic ground-state intermolecular potential energy calculations are often based on coupled cluster theory with a full treatment for single and double excitations and non-iterative perturbative treatment for triple excitations (CCSD(T)) [26–28], which is often called the ‘golden rule’ of theoretical chemistry computation. Although Møller–Plesset perturbation theory was very popular in the past (indeed, it is still quite popular now), in the field of intermolecular interactions, matching the ever more accurate experimental data requires more accurate calculations. In particular, the basis set used is very important, and for describing intermolecular properties at large monomer–monomer separations, ‘augmentation’ of the basis set is necessary. This has led to the use of Dunning’s augmented correlation-consistent basis sets [29], aug-cc-pVXZ ( $X = T, Q, 5 \dots$ ). Mid-bond functions, which are particularly useful for the computation of Rydberg states, are often also used to facilitate computational convergence [30]. The resulting ‘Supermolecule’ method is easy to use and understand. It allows the intermolecular interaction between molecules A and B to be written as

$$\Delta V(\mathbf{r}_A, \mathbf{r}_B; \mathbf{\Omega}) = E_{A \dots B}(\mathbf{r}_A, \mathbf{r}_B; \mathbf{\Omega}) - E_A(\mathbf{r}_A) - E_B(\mathbf{r}_B), \quad (1)$$

in which  $\mathbf{\Omega}$  denotes the relative position (and orientation) of molecules A and B, and  $E_{A \dots B}$ ,  $E_A$  and  $E_B$  are, respectively, the energies of the vdW complex and of the isolated molecules, which can be directly obtained from the electronic structure calculations. Note that the intermolecular interaction is also a function of intramolecular coordinates ( $\mathbf{r}_A$  and  $\mathbf{r}_B$ ). However, it should be clarified that the energy change corresponding to the potential within the monomer molecules themselves, rather than to the intermolecular interaction, is not a part of the intermolecular PES. To minimise the basis set superposition error, the full counterpoise procedure is often employed for size-consistent methods such as the CC theory.

Recently, explicitly correlated methods [31,32] have often been used to accelerate electronic structure calculations. In particular, the CCSD(T)-F12/aug-cc-pVTZ method/basis set has frequently been used in the study of vdW complexes in recent years. When this kind of strategy has been compared with traditional methods using a ‘large enough’ basis set or a complete basis set, it has been proved to be effective [33–36].

## 3. A brief review of the 1D Morse/Long-Range (MLR) model

Although it is not the theme of this review, a brief introduction to the 1D MLR model is presented here to provide the reader with sufficient knowledge to understand the mdMLR function described in the following sections.

The MLR potential energy model is a relatively new one which was developed only in the twenty-first century. A primitive version of this model was first described in 2006 in an application determining a potential for  $N_2$  [23]. It was then formally defined and characterised in the course of a 2007 application to ground-state  $Ca_2$  [24]. The most recent version of the MLR form is basically that used in a study of two electronic states of  $Li_2$  [25], and an optional ‘damping function’ was later added in 2010 which serves to improve both the long- and short-range behaviours [37]. The MLR model is still actively under development by Professor Le Roy and co-workers, as has been reported in several conference proceedings.

The current version of the 1D MLR model has the form

$$V_{MLR}(R) = \mathcal{D}_e \left\{ 1 - \frac{u_{LR}(R)}{u_{LR}(R_e)} e^{-\beta(R) \cdot y_p^{eq}(R)} \right\}^2 - \mathcal{D}_e + V_{lim}, \quad (2)$$

in which  $\mathcal{D}_e$  is the well depth,  $R_e$  the equilibrium internuclear separation and  $V_{lim}$  a specified value for the absolute energy at the asymptote. The function  $u_{LR}(R)$  represents the ‘long-range interaction’, and is usually written as

$$u_{LR}(R) = D_{m_1}(R) \frac{C_{m_1}}{R^{m_1}} + D_{m_2}(R) \frac{C_{m_2}}{R^{m_2}} + \dots + D_{m_{last}}(R) \frac{C_{m_{last}}}{R^{m_{last}}}, \quad (3)$$

where  $D_{m_i}(r)$  are optional user-selected damping functions, which may have various forms [37], and the  $C_{m_i}$  coefficients are normally defined by perturbation theory. This long-range function should be specified in advance, because it defines the physically meaningful behaviour of the system at large  $R$ . The dimensionless exponent radial variable  $y_p^{eq}(R)$  maps  $R \in [0, +\infty)$  onto the finite domain  $y_p \in [-1, 1]$ , and is written as

$$y_p^{eq}(R) = \frac{R^p - R_e^p}{R^p + R_e^p}. \quad (4)$$

The exponent coefficient function  $\beta(R)$  in Equation (2) is then normally written as a constrained power series in a radial variable that has the same form as Equation (4), but which differs in that the power  $p$  is replaced by a power  $q$ , and a user-defined reference distance  $R_{ref}$  replaces  $R_e$  the

expansion centre:

$$\beta(R) = y_p^{\text{ref}}(R) \beta_\infty + [1 - y_p^{\text{ref}}(R)] \sum_{i=0}^{N_\beta} \beta_i y_q^{\text{ref}}(R)^i. \quad (5)$$

Here,  $y_p^{\text{ref}}(R)$ , which again has the same structure as Equation (4) and is defined by the same power that defines that radial variable, but the same reference distance as the expansion variable  $y_q^{\text{ref}}(R)$ , is a switching function constraining  $\beta(R)$  to approach the specified asymptotic value  $\lim_{R \rightarrow \infty} \beta(R) \equiv \beta_\infty = \ln[2\mathcal{D}_e/u_{\text{LR}}(R_e)]$ .

This MLR radial potential energy form is easily usable due to published software implementations for either fitting it to a set of potential energy points using program `betaFIT` [38], or in direct fits to spectroscopic data using program `dPotFit` [39].

## 4. Expanding the MLR model to handle inter-molecular interactions

### 4.1. The potential energy function form

If one separates out any *strong* electrostatic interactions due to permanent multipole moments on the interacting monomers,  $V_{\text{elst}}(R, \mathbf{\Omega})$ , the interaction potential energy between two rigid molecules may be written as

$$\Delta V = V_{\text{vdW}}(R, \mathbf{\Omega}) + V_{\text{elst}}(R, \mathbf{\Omega}), \quad (6)$$

where  $R$  is the distance between their centres-of-mass and  $\mathbf{\Omega}$  the set of angles that defines their relative orientation. The central *ansatz* of the mdMLR model is that the first term in Equation (6) has a simple Morse-like potential well whose depth, radial position and shape vary smoothly (and often slowly) with  $\mathbf{\Omega}$ . In some cases, it may be possible to incorporate the electrostatic terms within a generalised analytic expression for the long-range part of the vdW component of the interaction potential

$$u_{\text{LR}}(R; \mathbf{\Omega}) = D_{m_1}(R) \frac{C_{m_1}(\mathbf{\Omega})}{R^{m_1}} + D_{m_2}(R) \frac{C_{m_2}(\mathbf{\Omega})}{R^{m_2}} + \dots + D_{m_{\text{last}}}(R) \frac{C_{m_{\text{last}}}(\mathbf{\Omega})}{R^{m_{\text{last}}}}. \quad (7)$$

However, if the electrostatic terms are sufficiently strong, the resulting  $V_{\text{vdW}}(R, \mathbf{\Omega})$  function would have no radial minima for some values of  $\mathbf{\Omega}$ , and the approach proposed herein would not be applicable.

As is implied by its name, the mdMLR potential represents the radial behaviour of  $V_{\text{vdW}}(R, \mathbf{\Omega})$  along a cut at

any particular value of  $\mathbf{\Omega}$  by the following generalised version of Equation (2):

$$V_{\text{mdMLR}}(R; \mathbf{\Omega}) = \mathcal{D}_e(\mathbf{\Omega}) \left\{ 1 - \frac{u_{\text{LR}}(R; \mathbf{\Omega})}{u_{\text{LR}}(R_e(\mathbf{\Omega}); \mathbf{\Omega})} e^{-\beta(R; \mathbf{\Omega}) \cdot y_p^{\text{eq}}(R; \mathbf{\Omega})} \right\}^2 - \mathcal{D}_e(\mathbf{\Omega}) + V_{\text{lim}}, \quad (8)$$

in which  $\beta(R; \mathbf{\Omega})$  is a generalised version of Equation (5) in which the expansion coefficients  $\beta_i(\mathbf{\Omega})$  are also functions of the orientation angles. The well of depth  $\mathcal{D}_e(\mathbf{\Omega})$ , equilibrium distance  $r_e(\mathbf{\Omega})$  ‘shape’ parameters  $\beta_i(\mathbf{\Omega})$  and long-range coefficients  $C_{m_i}(\mathbf{\Omega})$  are then expanded as linear combinations of an appropriate set of orthogonal angular basis functions, and those expansion coefficients are the fitting parameters defining the potential.

### 4.2. Fitting strategy

Non-linear least-square fitting is the essential technology for determining the desired multi-dimensional analytic mdMLR potential energy function. As in any non-linear least-square fitting, it is essential to obtain realistic initial trial estimates of the fitting parameters. To this end, tools that were developed for the 1D diatomic molecule case have proved to be very useful.

Along a cut at any particular set of angles  $\mathbf{\Omega}_j$ , the vdW part of the PES may be represented by the 1D MLR potential of Equation (2), and in practice, this usually requires only a small number of exponent expansion coefficients,  $\beta_i(\mathbf{\Omega}_j)$ . However, fitting Equation (2) to that 1D radial behaviour is itself a non-linear least-squares problem that requires realistic starting parameters. Fortunately, this problem has been addressed for this 1D case by the approximate linearisation incorporated within the program `betaFIT` [38]. The resulting sets of parameter values  $\mathcal{D}_e(\mathbf{\Omega}_j)$ ,  $R_e(\mathbf{\Omega}_j)$ ,  $\beta_i(\mathbf{\Omega}_j)$  and  $C_m(\mathbf{\Omega}_j)$  for a range of angles  $\mathbf{\Omega}_j$  may then each be fitted in a *linear* least-squares fit as functions of the angles  $\mathbf{\Omega}_j$ , and those expansion coefficients will provide a realistic initial approximation to the desired final global multi-dimensional vdW PES.

As with the 1D MLR model, the long-range coefficients in the mdMLR model (now functions of the angles  $\mathbf{\Omega}$ ) should be specified in advance. There are theoretical methods that can compute the values of those long-range coefficients, such as the symmetry-adapted perturbation theory [7], which can directly provide the dispersion and induction coefficients which define the main part of the long-range interaction. However, rather than work with such theories, an easier way to obtain the desired long-range coefficients may be to perform what we call ‘long-range fitting’. In this case, it is usually convenient to omit



the damping functions and replace Equation (3) by

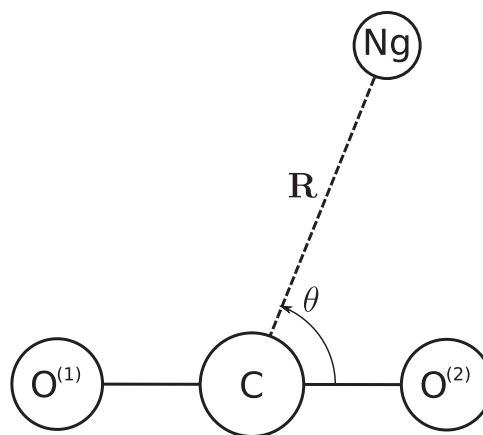
$$u_{\text{LR}}(R; \boldsymbol{\Omega}) = \frac{C_{m_1}(\boldsymbol{\Omega})}{R^{m_1}} + \frac{C_{m_2}(\boldsymbol{\Omega})}{R^{m_2}} + \dots + \frac{C_{m_{\text{last}}}(\boldsymbol{\Omega})}{R^{m_{\text{last}}}}. \quad (9)$$

At long range, those damping functions tend to have values close to 1, and adaptation of the recommended forms [37] of  $D_m(R)$  to the multi-dimensional case would at best be somewhat ad hoc, so this simplification is reasonable. Turning points obtained from large- $R$  *ab initio* calculations for a particular set of angles  $\boldsymbol{\Omega}_j$ , often with  $R \gtrsim 7 \text{ \AA}$ , for example, are fitted to Equation (9). The coefficients obtained from these *linear* fits would then be held fixed in the subsequent *non-linear* fit of Equation (2) to the full radial potential along the cut for that particular value of  $\boldsymbol{\Omega}_j$ . Note, however, that coefficients of the leading long-range terms, especially any weak electrostatic terms that did not have to be separated out in  $V_{\text{elst}}(R, \boldsymbol{\Omega})$ , often have known angular and radial behaviour, and may be included directly as known terms in Equation (9).

Once the sets of angular expansion parameters for each of the mdMLR's radial parameters have been obtained from those linear least-squares fits to a set of orthogonal functions of  $\boldsymbol{\Omega}$ , the final global *non-linear* fittings may then be performed. In those final fits, it may be appropriate to adjust the uncertainties (weights) of different sets of turning points. Our recommended approach is to weight all points at energies below the asymptote  $V_{\text{lim}}$  equally, while points higher on the repulsive wall are weighted by ever greater uncertainties.

## 5. Multi-dimension MLR potential energy surfaces

The first PES built with an mdMLR model was that of Li and Le Roy for the  $\text{CO}_2\text{-He}$  system, where three dimensions were taken into consideration: the intermolecular distance  $R$ , the orientation of the  $\text{CO}_2$  molecule  $\theta$  and the intramolecular asymmetric-stretch vibrational normal coordinate  $Q_3$  [40]. In this case, there was only a single relative orientation angle, and the dependence on  $Q_3$  led to the definition of separate two-dimensional surfaces for the two lowest  $\nu_3$  vibrational levels of  $\text{CO}_2$ , with their asymptotes separated by the vibrational energy of the free  $\text{CO}_2$  monomer. Based on this PES, the IR spectrum of  $\text{CO}_2\text{-He}$  complex around  $2349 \text{ cm}^{-1}$  was predicted and it agreed well with experimental data [40]. Moreover, when the effect of the  $\nu_3$  vibrational stretching on the average C-O bond length was taken into account (making this almost a four-dimensional (4D) PES), the observed  $\nu_3$  vibrational frequency shifts for  $\text{CO}_2\text{-He}_n$  clusters for  $n$  up to 40 were predicted correctly [22].



**Figure 1.** Geometry of  $\text{CO}_2\text{-Ng}$ . The two intermolecular coordinates are  $R$  and  $\theta$ .

The extensions of the mdMLR form to accommodate vibrational excitation and stretching of the component monomers are beyond the scope of this review. We note, however, that accounting for the stretching associated with intramolecular vibration in one or both of the component monomer(s) is essential if one wishes to account quantitatively for the IR spectra of complexes.

In the present discussion, the mdMLR model will be classified in terms of the rotational degrees of freedom of the two interacting monomers which may include: (i) an atom, (ii) linear molecules and/or (iii) non-linear molecules. The classification is based on the fact that the angular basis functions are different for these different cases.

### 5.1. Atom plus linear-molecule complexes

Noble gas (Ng) atoms are found in many spectroscopically studied vdW complexes. Helium is the complexing partner in the largest number of cases, and its complexes are also often present when it is used as a coolant in investigations involving *para*-hydrogen. The mdMLR model for a system composed of an atom with a rigid linear molecule has two intermolecular degrees of freedom: the magnitude of the vector pointing from the linear molecule to the atom, and the angle between this vector and a vector pointing along the axis of the molecule. One example of this kind of complex is  $\text{CO}_2\text{-He}$  [40], whose structure is shown and coordinates defined in Figure 1.

In the mdMLR model, the orthogonal functions, in terms of which the MLR radial parameters are expanded, are the Legendre polynomials  $P_\lambda(x)$ , which may be written as

$$P_\lambda(x) = \frac{1}{2^\lambda \lambda!} \frac{d^\lambda}{dx^\lambda} [(x^2 - 1)^\lambda], \quad (10)$$

in which  $x = \cos \theta$ . Hence, in the mdMLR function, the parameter  $\mathfrak{D}_e(\Omega)$ , for example, is expanded as

$$\mathfrak{D}_e(\theta) = \sum_{\lambda} \mathfrak{D}_e^{(\lambda)} \cdot P_{\lambda}(\cos \theta), \quad (11)$$

and similar expressions are employed for  $R_e(\theta)$ ,  $\beta_i(\theta)$  and  $C_{m_i}(\theta)$ .

In Ref. [40], the authors actually accomplished a more complicated task by explicitly including the antisymmetric stretching coordinate ( $Q_3 \equiv \frac{\sqrt{2}}{2}[r_{\text{CO}^{(1)}} - r_{\text{CO}^{(2)}}]$ ) of  $\text{CO}_2$  in the final analytic PES. In that case, the intermolecular interaction was a function of three variables:  $R$ ,  $\theta$  and  $Q_3$ . A 1D MLR was still used to define the radial behaviour, but all of its parameters were functions of  $(\theta, Q_3)$ , with expansions in Legendre polynomials being used to represent the angular behaviour while the small changes due to  $Q_3$  were accounted for by a power series expansion in  $Q_3$ . The total basis functions of such systems were therefore

$$\phi_{\lambda,n}(\theta, Q_3) = P_{\lambda}(\cos \theta) \cdot Q_3^n. \quad (12)$$

The parameters of the mdMLR were therefore expanded as (for example)

$$\mathfrak{D}_e(\theta) = \sum_{\lambda,n} \mathfrak{D}_e^{(\lambda,n)} \cdot P_{\lambda}(\cos \theta) Q_3^n. \quad (13)$$

Of course, the symmetry of this system means that

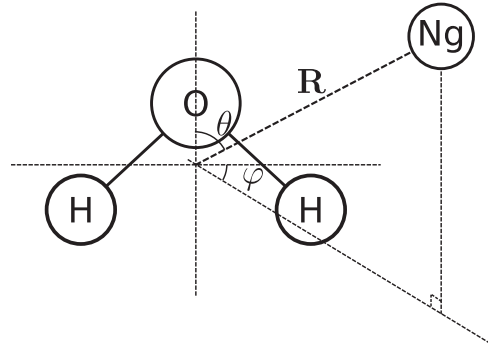
$$\Delta V(R, \theta, Q_3) = \Delta V(R, \pi - \theta, -Q_3), \quad (14)$$

which in turn means that the non-zero terms in Equation (13) must obey the condition that  $\lambda + n$  be an even number. For the simpler case in which the intramolecular vibrational coordinates are not included, the values of  $\lambda$  are restricted to be even numbers.

Another illustrative atom-plus-linear-molecule system is  $\text{OCS-He}$  [21]. To define its geometry,  $\text{O}^{(2)}$  in Figure 1 is replaced with S and the origin is shifted to the centre of mass of the OCS. The basis functions used in describing the  $\text{OCS-He}$  interaction were then the same as those for  $\text{CO}_2\text{-He}$  (Equation (11)), except that the requirement that  $\lambda$  (or more generally,  $\lambda + n$ ) be even is lifted.

## 5.2. Atom plus non-linear-molecule complexes

Water is probably the molecule of most interest to the community, not only because of its central role in chemical reactions under aqueous condition, including those supporting life, but also because of its interesting physical properties, such as the spectroscopy of its complexes.



**Figure 2.** Geometry of  $\text{H}_2\text{O-He}$ . The three atoms of  $\text{H}_2\text{O}$  lie in the plain of the paper while helium can be out of it. The intermolecular variables are  $R$ ,  $\theta$  and  $\varphi$ .

As a result, water-Ng complexes are paradigm systems in the study of inter- and intra-molecular coupling. Theoretical understanding of the rovibrational properties of water-Ng complexes begins with the construction of an intermolecular PES in which the intramolecular vibrational coordinates are explicitly taken into consideration. In the development of the mdMLR model, the water-Ng complex used as the representative atom plus non-linear-molecule system is shown in Figure 2.

In this case, the potential can be expanded in terms of the tesseral spherical harmonic functions

$$Y_{\ell m}(\theta, \varphi) = \begin{cases} \sqrt{2} \sqrt{\frac{(2\ell+1)(\ell-\bar{m})!}{4\pi(\ell+\bar{m})!}} P_{\ell}^{\bar{m}}(\cos \theta) \sin \bar{m}\varphi & \text{if } m < 0 \\ \sqrt{\frac{(2\ell+1)}{4\pi}} P_{\ell}^m(\cos \theta) & \text{if } m = 0 \\ \sqrt{2} \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_{\ell}^m(\cos \theta) \cos m\varphi & \text{if } m > 0 \end{cases} \quad (15)$$

in which  $\bar{m}$  stands for  $-m$  and  $P_{\ell}^m(\cos \theta)$  are the so-called associated Legendre polynomials

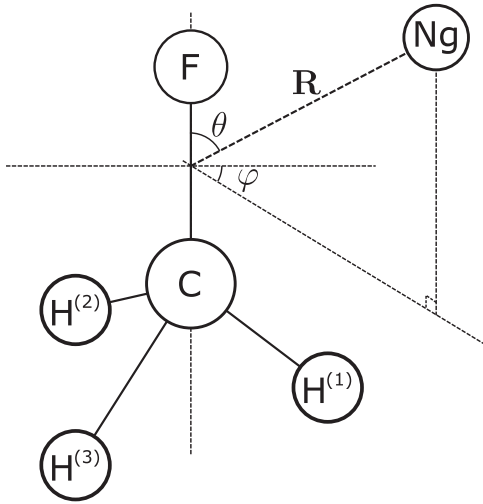
$$P_{\ell}^m(x) = (-1)^m (1-x^2)^{m/2} \frac{d}{dx} P_{\ell}(x). \quad (16)$$

For symmetry reasons, the expansions for the parameters of the mdMLR are written as

$$\mathfrak{D}_e(\theta, \varphi) = \sum_{\ell} \sum_{m=0}^{\ell} \mathfrak{D}_e^{(\ell m)} \cdot Y_{\ell m}(\theta, \varphi), \quad (17)$$

and similar expressions are employed for  $R_e(\theta, \varphi)$ ,  $\beta_i(\theta, \varphi)$  and  $C_{m_i}(\theta, \varphi)$ .

The symmetry of  $\text{H}_2\text{O}$  is also taken into account in our model.  $\text{H}_2\text{O}$  is governed by the  $C_{2v}$  point group, and its



**Figure 3.** Geometry of  $\text{CH}_3\text{F-Ng}$ . The three atoms C, F and  $\text{H}^{(1)}$  of  $\text{CH}_3\text{F}$  lie in the plain of the paper and helium can be out of it. The intermolecular variables are  $R$ ,  $\theta$  and  $\varphi$ .

angular basis functions belong to the  $A_1$  irreducible representation and hence obey the requirement that

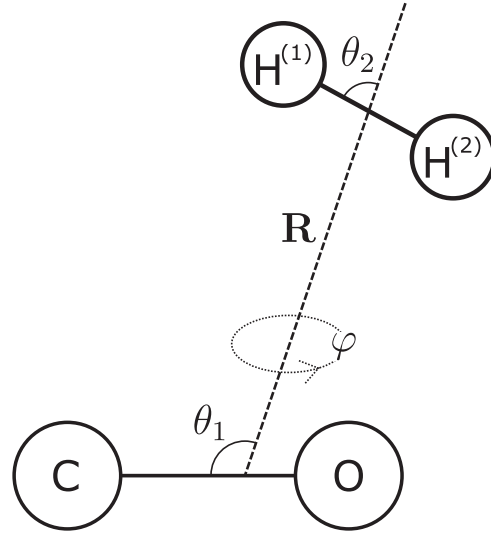
$$\ell \geq 0, \quad \text{mod}(m, 2) = 0. \quad (18)$$

This model can be used for other atom plus non-linear-molecular systems if one remembers to take account of the relevant symmetry.  $\text{CH}_3\text{F-Ng}$  ( $\text{Ng} = \text{He}$ ,  $\text{Ne}$  and  $\text{Ar}$ , see Figure 3) are also interesting subjects because the IR spectrum of  $\text{CH}_3\text{F}$  was first measured in 1928 [41], and it has frequently been used as a probe in IR spectroscopy research. When dealing with the  $\text{CH}_3\text{F-Ng}$  system [42–44], one can use the same expansions of Equation (17), while taking account of the symmetry. Since  $\text{CH}_3\text{F}$  belongs to  $C_{3v}$  point group, the potential should be in the  $A_1$  irreducible representation, which means that the basis function used will be subject to the restriction that

$$\ell \geq 0, \quad \text{mod}(m, 3) = 0. \quad (19)$$

### 5.3. Linear-molecule plus linear-molecule complexes

*Para*-hydrogen ( $p\text{H}_2$ ) is the only superfluid substance other than helium [45,46]. As a probe of the superfluidity of  $p\text{H}_2$ , a rotor chromophore may be doped into  $p\text{H}_2$  clusters, and IR and MW spectroscopy used to examine its surroundings. For theoretical studies of this type, PESs for rotor–hydrogen complexes are required. Among them, linear molecule– $p\text{H}_2$  complexes are the simplest and most frequently studied. In such linear-molecule plus



**Figure 4.** Geometry of  $\text{CO-H}_2$ . Intermolecular variables are  $R$ ,  $\theta_1$ ,  $\theta_2$  and  $\varphi$ .

linear-molecule complexes, at least four degrees of freedom are required to describe the potential; see Figure 4.

The angular basis function for describing the PESs of linear-molecule plus linear-molecule complexes has the form

$$A_{\ell_1 \ell_2 \ell}(\theta_1, \theta_2, \varphi) = \sum_{m=-\ell_{\min}}^{\ell_{\min}} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ m & \bar{m} & 0 \end{pmatrix} Y_{\ell_1 m}(\theta_1, 0) Y_{\ell_2 \bar{m}}(\theta_2, \varphi), \quad (20)$$

in which  $\ell_{\min} = \min(\ell_1, \ell_2)$  and the triangle relation requires that  $|\ell_1 - \ell_2| \leq \ell \leq |\ell_1 + \ell_2|$ . In view of the symmetry requirements that the potential must obey

$$\Delta V(R, \theta_1, \theta_2, \varphi) = \Delta V(R, \theta_1, \pi - \theta_2, -\varphi), \quad (21)$$

we also have the constraints that

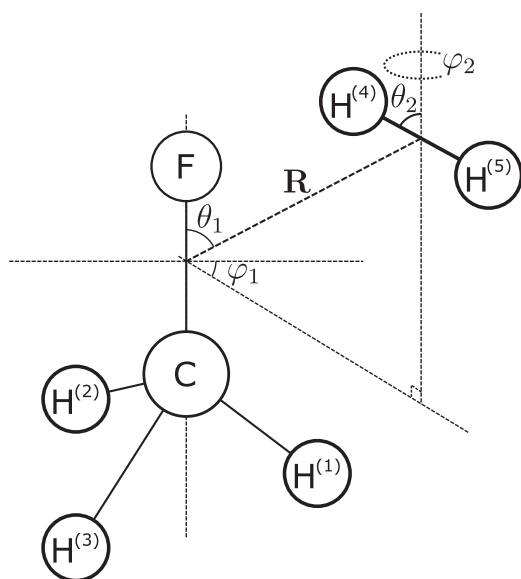
$$\begin{aligned} \ell_1, \ell_2, \ell &\geq 0, \\ \text{mod}(\ell_2, 2) &= 0 \\ \text{and } \text{mod}(\ell_1, 2) &= \text{mod}(\ell, 2), \end{aligned} \quad (22)$$

to apply to the basis functions.

### 5.4. Non-linear-molecule plus linear-molecule complexes

The interaction between the two molecules in  $\text{CH}_3\text{F-H}_2$  is fundamental for understanding the properties of  $\text{CH}_3\text{F}$  embedded in solid  $p\text{H}_2$  [47]. The non-linear plus linear-molecule rigid-body interaction potential for this complex is a new type that has been devised quite recently [48]. The angular basis functions are





**Figure 5.** Geometry of  $\text{CH}_3\text{F}-\text{H}_2$ . The intermolecular coordinates are  $R, \theta_1, \theta_2, \varphi_1$  and  $\varphi_2$ .

super-spherical functions depending on the four angular variables defined in Figure 5, and have the form

$$\begin{aligned}
 & t_{\ell_1 m_1 \ell_2 \ell}(\theta_1, \theta_2, \varphi_1, \varphi_2) \\
 &= [2(1 + \delta_{m_1 0})^{-1} (2\ell_1 + 1)^{-1}]^{-1/2} (1 + \delta_{m_1 0})^{-1} \\
 &\times \sum_{r_1 r_2} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ r_1 & r_2 & r \end{pmatrix} Y_{\ell_2 r_2}(\theta_2, \varphi_2) Y_{\ell r}(\theta_1, \varphi_1) \\
 &\times [\delta_{m_1 r_1} + (-1)^{\ell_1 + m_1 + \ell_2 + l} \delta_{\bar{m}_1 r_1}]. \quad (23)
 \end{aligned}$$

For symmetry reasons, the indices of these functions must obey the condition that

$$\text{mod}(m, 3) = 0 \quad \text{and} \quad \text{mod}(\ell_1 + \ell_2 + \ell, 2) = 0. \quad (24)$$

### 5.5. Applications of the mdMLR model

A summary of currently published applications of the mdMLR model in the study of vdW complexes is presented in Table 1. It is clear that increases in dimensionality give rise to marked increases in the number of required expansion parameters. This is mainly due to the fact that more complex monomer shapes require more terms in the *linear* expansions of Equations (13) or (17), or the analogous expressions based on the higher-order angular basis functions of Equations (20) or (23), for each of the modest number of parameters required to define the radial behaviour. In all cases, the fitted potentials can provide predictions with spectroscopic precision. In particular, if the *ab initio* calculation is reliable, an mdMLR potential can accurately reproduce the level energies implied by the quantum chemistry calculation with a portable and fully analytic PES. Moreover, when appropriate internal-mode ‘vibrational averaging’ is combined with very high-level quantum chemistry results, the MW and IR spectra predictions generated from the mdMLR PES always agree closely with the available experimental data. For example, the work in Ref. [49] accurately predicted both the line positions and line strengths in the IR spectrum of the  $\text{OCS}-\text{H}_2$  complex, and the calculated IR spectra based on the analytical

**Table 1.** Overview of published mdMLR PESs. Column 3 lists the number of *ab initio* points fitted to the mdMLR form, Column 4 the root-mean-square deviation (RMSD) of that fit and Column 5 the number of mdMLR fitting parameters.

Complex	Dimension	Number of points	RMSD ( $\text{cm}^{-1}$ )	Number of parameters	Ref.
1. Linear molecule–atom					
$\text{CO}_2-\text{He}$	3	2832	0.032	55	[40]
$\text{OCS}-\text{He}$	2	305	0.022	49	[21]
$\text{N}_2\text{O}-\text{He}$	4	21,390	0.763	592	[50]
2. Non-linear molecule–atom					
$\text{H}_2\text{O}-\text{He}$	3	578	0.1	53	[51]
$\text{H}_2\text{O}-\text{Ar}$	3	442	0.15	58	[52]
$\text{H}_2\text{O}-\text{Ne}$	3	646	0.12	56	[53]
$\text{CH}_3\text{F}-\text{He}$	3	3150	0.05	102	[42]
$\text{CH}_3\text{F}-\text{Ar}$	3	2038	0.08	120	[43]
$\text{CH}_3\text{F}-\text{Ne}$	3	2340	0.07	167	[44]
3. Linear molecule–linear molecule					
$\text{CO}_2-\text{H}_2$	4	23,113	0.143	167	[54]
$\text{CO}-\text{H}_2$	4	30,206	0.087	196	[55]
$\text{N}_2\text{O}-\text{H}_2$	4	2188	0.133	255	[56]
$\text{OCS}-\text{H}_2$	4	13,485	0.16	358	[49]
4. Non-linear molecule–linear molecule					
$\text{CH}_3\text{F}-\text{H}_2$	5	25,025	0.74 <sup>a</sup>	823	[48]

<sup>a</sup>This RMSD reduces to 0.082 for interaction energy less than 0.

4D mdMLR for both vibrational ground- and excited-states of OCS agree with the experimental values with mean differences less than  $0.01\text{cm}^{-1}$  for all five (spin) isotopologues.

Data involving low-lying rovibrational energy levels only test the nature of a PES near its minimum. However, as is implied by its name, the physically correct long-range behaviour built into the mdMLR model means that a PES fitted to this form will also behave realistically at large distances. This is confirmed by the vibrational frequency shifts predictions for  $\text{OCS}-(\text{He})_n$  clusters for a wide range of cluster sizes, in which the outermost atoms are ever farther from the chromophore probe [21]. In particular, quantum Monte Carlo simulation based on a two-body summation PES shows that up to the largest cluster size for which data are available,  $n = 72$ , the mdMLR PES gives predicted IR frequency shifts in very close agreement with the experiment. Analogous results for slightly smaller clusters were obtained earlier for the  $\text{CO}_2-(\text{He})_n$  system [22].

Note that for all of the multi-dimensional PESs listed in Table 1, a compact portable FORTRAN subroutine for generating its value at any specified configuration was made available as supplementary data associated with the original paper. For the convenience of users, these subroutines are all also available at <http://huiligroup.org/mdMLR/>. This site will also host programs for performing linear least-squares fits of the type associated with Equations (13) or (17) and the analogous expressions based on the higher-order angular basis functions of Equations (20) or (23) and for performing the final full non-linear least-squares fits to the resulting models.

## 6. Discussion and outlook

The efficacy of the mdMLR model seems to be extremely good, and it clearly can be applied to a wide range of vdW complexes. However, some of its limitations are also quite evident. In particular, the requirement that realistic long-range coefficients must be known or be estimated is a significant ‘damping’ consideration that restricts ‘flippant’ applications of this approach, a restriction that does not apply to the case of NNPEs. Although efforts have been made to facilitate our fitting procedure, the total operations included are still somewhat complex.

Unlike some of the other models, the mdMLR approach described herein also requires the mesh of *ab initio* intermolecular energies to be laid out on a regular grid. In particular, results for all relative monomer orientations must be available at precisely the same grid of radial distances, and the points along that grid must suffice to define a realistic 1D MLR PEC along each cut. This

means that the PES cannot readily be a by-product of simulation technologies such as *ab initio* molecular dynamics. However, because this type of PES is used in follow-up rigid-body dynamics calculation such as rovibrational Schrödinger equation-solving or rigid-body (quantum) Monte Carlo or molecular dynamics simulations, the large up-front cost of constructing an intermolecular PES in this way is quite acceptable.

‘Vibrational averaging’ is one of the most important considerations in the construction of the PES of a vdW complex. It is the nature of the molecules that they *always* vibrate, and the resulting phenomenon, zero point energy, is one of the most important quantum mechanical effects in molecular science. It means, for example, that the bond length(s) that should be associated with a molecule in its ground state are usually *not* the same as those associated with the ‘equilibrium configuration’ at the minimum of the PES, particularly for bonds involving light atoms such as H and its isotopes. This should be taken into account in defining the monomer structure(s) used in rigid-molecule PES calculations. While determining the appropriate bond length is a simple matter for diatomic monomers (though it is *not* the distance associated with the ground-state inertial rotational constant, as is often assumed), it is of course more difficult for polyatomic components. However, for systems such as  $\text{CO}_2-(\text{He})_n$ ,  $\text{OCS}-(\text{He})$  or  $\text{CO}_2-(p\text{H}_2)_n$ , it has been shown that it is essential to take account of vibrationally averaged monomer bond-stretching if one wishes to account for the vibrational frequency shifts in the larger clusters.

It is also clear that the higher the dimensionality is, the more challenging the fitting becomes. From our experience to date, we find that to achieve high accuracy, many parameters are required for  $\mathcal{D}_e(\Omega)$ ,  $R_e(\Omega)$  and  $\beta_0(\Omega)$ , while with sharply smaller numbers of parameters being required for the higher-order exponent coefficients  $\beta_i(\Omega)$  ( $i \geq 1$ ). However, the fitting strategy described in Section 4.2 makes the method virtually as robust and straightforward as for the 1D case, although one usually has to tinker with the numbers of angular terms associated with each MLR angular parameter.

To date, the mdMLR model has not been applied to excited electronic state of vdW complexes. Molecules with degenerate ground electronic states interacting with a quantum solvent such as He or  $p\text{H}_2$  should provide a good test of the flexibility of both the mdMLR and other intermolecular interaction potential models. Since the mdMLR model has already proved to be successful for the study of complexes involving molecules in different vibrational states, it is very likely that it will be useful for the projects mentioned above.

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No potential conflict of interest was reported by the authors.

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