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The extended Lennard-Jones potential energy function: A simpler model for direct-potential-fit analysis

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ABSTRACT

An analytical model for the diatomic potential energy function that was recently tested as a universal function (Hajigeorgiou, 2010) has been further modified and tested as a suitable model for direct-potential-fit analysis. Applications are presented for the ground electronic states of three diatomic molecules: oxygen, carbon monoxide, and hydrogen fluoride. The adjustable parameters of the extended Lennard-Jones potential model are determined through nonlinear regression by fits to calculated rovibrational energy term values or experimental spectroscopic line positions. The model is shown to lead to reliable, compact and simple representations for the potential energy functions of these systems and could therefore be classified as a suitable and attractive model for direct-potential-fit analysis.

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1. Introduction

The determination of a potential energy function (PEF) for a diatomic molecule from experimental information has long been a principal objective of molecular physics. During the era preceding and following the dawn of quantum mechanics by Heisenberg's matrix mechanics formulation in late 1925 [1], and through Schrödinger's wave mechanics representation in late 1926 [2], simple few-parameter closed-form PEFs were proposed by several investigators [3–6]. The concept of a PEF for an isolated non-interacting electronic state also emerges naturally from the theoretical treatment of Born and Oppenheimer [7], where separation of nuclear and electronic motions is achieved by assuming instantaneous adjustment of the electronic cloud in response to small changes in the internuclear spacing. Essentially, the electronic energy eigenvalues are calculated at fixed internuclear separations, and together with the nucleus-nucleus Coulombic repulsion term they comprise the traditional PEF. Generation of a PEF for a diatomic molecule is an efficient way to encapsulate the rovibrational energy levels and associated wavefunctions, and is particularly useful for further applications in chemical physics.

Owing to limited computational resources and given the relatively crude precision of spectroscopic information at the time, the simple available models for the potential energy were often adequate. However, over the years, the development of more advanced spectroscopic techniques and the associated improvement in the precision of spectroscopic data, along with the parallel enhancement of computational resources, led to the proposal of more refined schemes for the determination of a PEF. A numerical procedure that served as a reliable workhorse for many decades is the Rydberg-Klein-Rees (RKR) method [8–10], which is based on the 1st-order Wentzel-Kramers-Brillouin (WKB) quantization condition [11–13], a convenient framework leading to the solution of the Schrödinger equation for nuclear motions.

The wide availability of powerful microcomputer systems in recent decades has revolutionized the field of spectroscopic analysis. Estimation of molecular constants has been superseded by modern numerical methods, such that direct determination of multi-parameter PEFs from very highly precise spectroscopic data has nowadays become routine. A brief history of the evolution of advanced empirical models for the potential energy is considered below in this article. It is argued that while investigators have achieved superb modeling of the physical aspects of diatomic molecular electronic states, the increasing complexity of the models has rendered the end-products of such work far too unpalatable for most users. As an indication of the growing complexity of modern semi-empirical PEFs, it is worth emphasizing that key contributors to this type of analysis such as Coxon and Hajigeorgiou [14] and Le Roy's group [15] have recently included in supplementary material stand-alone Fortran subroutines for calculating the PEFs from sets of estimated parameters. The principal objective of the present work is to revert to a more comfortable level of simplicity

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in the PEF while still accounting for the various effects that govern the behavior of a chemical bond at different internuclear distances.

The PEF model proposed in the present work is a modified version of the Extended Lennard-Jones (ELJ) potential developed by Hajigeorgiou [16]. The ELJ model is applied in direct-potential-fit (DPF) analyses of three diatomic data sets: (a) rovibrational term values for the ground electronic state of oxygen, (b) a large set of spectroscopic line positions for the ground electronic state of carbon monoxide, and (c) all the available ground state pure rotational, vibrational-rotational and $B \rightarrow X$ electronic data for hydrogen fluoride. It is demonstrated that application of the ELJ model gives results that are fully comparable with those from previous analyses that employed either more complicated or structurally less adequate models for the PEF. The underlying simplicity of the ELJ model makes it a desirable option for DPF analysis.

2. Evolution of PEF models for DPF analysis

The first investigation employing a DPF analysis on diatomic systems was carried out in 1988 by Gruebele et al. on the ground electronic states of the cations OH^+ and ArH^+ [17]. The models selected to represent the PEFs included the Dunham potential polynomial expansion [18], the Simons-Parr-Finlan (SPF) potential polynomial expansion [19], and a Morse potential expansion similar to that proposed originally in Dunham's seminal paper [18]. While all three expansions gave asymptotically well-behaved functions, they failed to adhere to the theoretically expected ion-dipole C_4/r^4 dependence at long-range, which was in any case inconsequential since the spectroscopic data employed did not reach into the long-range region.

In 1990, Coxon and Hajigeorgiou [20] proposed the Generalized Morse Oscillator (GMO) model in the representation of numerical potential energy points, and employed this function successfully in subsequent DPF analyses on a variety of diatomic molecular states [21–23]. The basic structure of the GMO function was that of a Morse potential that incorporated a radial variation on the exponential parameter β. While this PEF form was successful at representing spectroscopic data to within the estimated experimental uncertainties, it had a built-in flaw that could lead to pathological behavior of a PEF extrapolated to large-r beyond the range of the experimental data, if the last fitted parameter of the $\beta(r)$ expansion was fortuitously negative. In addition, even in the case of no pathological behavior, the long-range potentials did not follow well-known theoretical behavior. Owing to these two important limitations, the GMO function does not possess the capability for reliable extrapolation to higher energies.

A more robust PEF was proposed by Dulick in 1993, in a series of publications from the Bernath group employing DPF methodology [24–26]. The modified Morse Oscillator (MMO) model served well in cases where the experimental data did not extend close to the dissociation limit of the potential well. In 1994, Hajigeorgiou and Le Roy [27] proposed a PEF model that simulated the expected long-range asymptotic behavior [28],

$$V(r) = \mathcal{D}_e - C_n/r^n. \tag{1}$$

where $\mathcal{D}_e$ is the dissociation energy of an electronic state, and C_n is the dispersion energy coefficient of the leading r^{-n} term in the long-range potential. The power n is determined with reference to the dissociation products of the electronic state in question. The modified Lennard-Jones (MLJ) model [29] was shown to possess the flexibility to represent effortlessly experimental information that reached up to 99% of the well depth in energy, in contrast to the MMO model, which was shown to lack adequate flexibility at higher energies. The MLJ model was employed successfully in a number of DPF analyses [30–34].

The next significant phase in the evolution of PEFs for DPF analyses was the development in 2006 (publication appeared in 2007) by Le Roy and Henderson [35] of the Morse/Long-Range (MLR) potential function that included extended long-range behavior. The MLR function was capable of modeling the multi-term long-range expansion [36],

$$V(r) = \mathcal{D}_e - C_{n_1}/r^{n_1} - C_{n_2}/r^{n_2} - \ldots, \tag{2}$$

and the model was employed in many subsequent DPF analyses [37–42]. In 2010, Coxon and Hajigeorgiou [43] undertook an extensive DPF analysis of the ground electronic state of the cesium dimer, Cs_2. These authors proposed a slightly modified and more flexible version of the MLR model, and labelled it the MLR3 model. The MLR3 model was highly successful at representing the experimental spectroscopic information available on the ground electronic state of Cs_2, but it integrated an extra degree of complication that required more time-consuming testing at the fitting stage.

The implementation of physically sound long-range behavior in PEF models according to Eq. (2) was discovered to lead to problems on the inner-limb, particularly when higher-order inverse-power dispersion energy terms were included. In order to resolve this problem, Le Roy et al. [44] proposed the inclusion of conventional dispersion term damping functions that reduced the effect of these terms on the short-range behavior of MLR-type functions. Although this eradicated the problems on the inner limb of the derived PEFs, it introduced further complexity in the PEF models. Damping functions were also employed in the recent analysis of hydrogen halide ground electronic states by Coxon and Hajigeorgiou [14] employing an analogously modified MLR3 model. By this stage in the development of PEFs for DPF work, it was felt necessary to provide in supplementary materials computer code for restituting the relevant radial functions, as it was clear that the PEF models had become somewhat unwieldy, such that significant effort and time would be required for PEF calculations by the average user. The extra degree of complexity also introduced additional parameters to the model. The increased sophistication appeared essential in order to model the physical behavior of the PEF to a high degree of accuracy and realism, albeit at the heavy cost of reduced simplicity.

In summary, then, analytical PEF models started with very simple flexible mathematical forms, but became progressively more complicated in order to simulate more realistically the various characteristics of the physics of a chemical bond. This defeated the primary purpose of employing fully analytical PEF models, and could be considered an unwelcome shortcoming of current DPF methodology. In the next two sections, where the ELJ model is described and tested, it is shown that it is possible to fit highly precise experimental spectroscopic information to a PEF that has a more satisfying level of simplicity than currently employed models.

3. The ELJ potential energy function

In 2010, Hajigeorgiou [16] proposed a simple modification of the classic $(2n,n)$ Lennard-Jones function by allowing for a radial variation of the normally constant power n, as in

$$V(r) = \mathcal{D}_e \left[1 - \left(\frac{r_e}{r}\right)^{n(r)}\right]^2, \tag{3}$$

where r_e is the equilibrium internuclear separation. The radial function $n(r)$ is herein modeled as,

$$n(r) = \left(\sum_{i=0}^{N} \rho_i \zeta^i\right) f_n(r) + n_1(1 - f_n(r)), \tag{4}$$

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