Bridging the gap between laboratory astrophysics and quantum chemistry: The concept of potential energy surfaces

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Abstract. An exotic molecular inventory exists in space. While some species have well-known terrestrial analogs, others are very reactive and can hardly survive in the laboratory timely to allow for their characterization. With an eye toward these latter, we highlight in this contribution the role of quantum chemistry in providing astrochemically relevant data where experiment struggles. Special attention is given to the concept of molecular potential energy surfaces (PESs), a key aspect in theoretical chemical physics, and the possible dynamical attributes taken therefrom. As case studies, we outline our current efforts in obtaining global PESs of carbon clusters. It is thus hoped that, with such an active synergy between theoretical chemistry and state-of-the-art experimental/observational techniques (the pillars to the modern laboratory astrophysics), scientists may gather the required knowledge to explain the origins, abundances and the driving force toward molecular complexity in the Universe.

Keywords. potential energy surfaces, quantum chemistry, laboratory astrophysics

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1. Context

The space between stars is not completely empty, but is filled with a very dilute gas and dust particles; the interstellar medium (ISM). Despite its nasty, seemingly unproductive conditions, the ISM harbors an exotic molecular inventory (Tielens 2013). Starting from the first identification of CH, CH^+, and CN, scientists are nowadays aware of the existence of ≈ 200 molecules (McGuire 2018). Notwithstanding, the number of as-yet unidentified spectral lines attributable to molecules is still astounding (Tielens 2013). Apart from the knowledge gathered by (astronomical) spectroscopic observations, the understanding of the dynamical aspects leading to such species is also of paramount importance. Although several (gas-phase/grain-surface) chemical networks with thousands of reactions have been proposed to explain molecular synthesis and abundances, a large fraction of such reactions have never been studied at all or at the conditions of the ISM so that their rate constants are estimated with large uncertainties (Agúndez & Wakelam 2013).

The ISM provides an unique environment in which chemistry can be studied under extreme conditions. Undoubtedly, it is much better at creating nearly isolated molecules than any experiment on Earth. This, together with the natural constraints in producing and analyzing such highly reactive species in the laboratory, unravels therefore the usefulness of quantum chemistry (Fortenberry 2017). What bridges the gap between these latter two is unavoidably the notion of potential energy surfaces (PESs) (Murrell *et al.* 1984). Within the adiabatic approximation (Born & Oppenheimer 1927), PESs describe the potential energy of a system in terms of the relative positions of atoms that make up this system. Such potentials carry precise information about the underlying species,
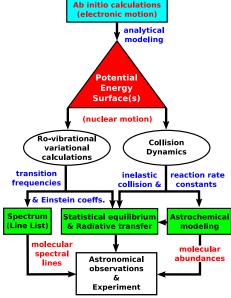
Figure 1. The molecular potential and its link to laboratory and astronomical observations.

and are important tools for the analysis of structural isomers, spectroscopy and reaction dynamics (Fig. 1). From the theoretical perspective, PESs are obtained by solving the electronic Schrödinger equation at sufficiently many (fixed) nuclear configurations whose energies are then modeled by some physically motivated analytic form. In so doing, one therefore is faced with the usefulness of such functional representations of PESs which can then be subject to nuclear motion problem, yielding dynamical attributes in which to compare and corroborate with experiment/observations.

2. The concept of potential energy surfaces

2.1. *Theoretical background*

In principle, the solution to the many-body problem can be found by means of the time-independent Schrödinger equation (Landau & Lifshitz 1981)

$$\hat{\mathcal{H}}_T \left| \Psi_n(\mathbf{r}, \mathbf{R}) \right\rangle = E_n \left| \Psi_n(\mathbf{r}, \mathbf{R}) \right\rangle, \qquad (2.1)$$

where $\hat{\mathcal{H}}_T$ is the non-relativistic Hamiltonian operator and $\left| \Psi_n(\mathbf{r}, \mathbf{R}) \right\rangle$ the total molecular wave function which depends on the set of all electronic $\mathbf{r}$ and nuclear $\mathbf{R}$ coordinates. In the absence of external time-varying fields, $\hat{\mathcal{H}}_T$ is then given by

$$\hat{\mathcal{H}}_T(\mathbf{r}, \mathbf{R}) = \hat{\mathcal{T}}_N(\mathbf{R}) + \hat{\mathcal{T}}_e(\mathbf{r}) + \hat{\mathcal{U}}(\mathbf{r}, \mathbf{R}), \qquad (2.2)$$

where $\hat{\mathcal{T}}_N(\mathbf{R})$ and $\hat{\mathcal{T}}_e(\mathbf{r})$ are the kinetic energy operators and $\hat{\mathcal{U}}(\mathbf{r}, \mathbf{R})$ the total potential energy. The adiabatic approximation assumes $\hat{\mathcal{T}}_N(\mathbf{R})$ as a small perturbation and in the limit of infinite nuclear masses, Eq. (2.2) takes the form (Born & Oppenheimer 1927)

$$\hat{\mathcal{H}}_e(\mathbf{r}; \mathbf{R}) = \hat{\mathcal{T}}_e(\mathbf{r}) + \hat{\mathcal{U}}(\mathbf{r}; \mathbf{R}), \qquad (2.3)$$

where $\hat{\mathcal{H}}_e(\mathbf{r}; \mathbf{R})$ is the electronic (clamped-nuclei) Hamiltonian that depends parametrically on $\mathbf{R}$. The problem of finding the stationary states of the system reduces then to solving the time-independent electronic Schrödinger equation (Landau & Lifshitz 1981)

$$\hat{\mathcal{H}}_e \left| \psi_i(\mathbf{r}; \mathbf{R}) \right\rangle = V_i(\mathbf{R}) \left| \psi_i(\mathbf{r}; \mathbf{R}) \right\rangle \qquad (2.4)$$

for fixed values of nuclear coordinates $\mathbf{R}$. In (2.4), $|\psi_i(\mathbf{r};\mathbf{R})\rangle$ are electronic adiabatic eigenfunctions that characterize states of motion of electrons for infinitely slow (adiabatic) changes in $\mathbf{R}$. $V_i(\mathbf{R})$ is the associated electronic eigenvalues and, if all possible sets of nuclear coordinates are considered, represents the effective PES for the nuclear motion. By expanding now $|\Psi_n(\mathbf{r},\mathbf{R})\rangle$ [Eq. (2.1)] in terms of the complete set $\{|\psi_i(\mathbf{r};\mathbf{R})\rangle\}_{i=1}^{\infty}$, one then gets [after some approximations (Born & Oppenheimer 1927)]

$$\left[\hat{\mathcal{T}}_N(\mathbf{R}) + V_i(\mathbf{R}) - E_n\right]|\chi_i(\mathbf{R})\rangle = 0, \tag{2.5}$$

which characterizes states of motion of the nuclei (with eigenfunctions $|\chi_i(\mathbf{R})\rangle$ and eigenvalues E_n) on the effective PES $V_i(\mathbf{R})$.

2.2. *Calculation & analytic representation of PESs*

A common starting point to obtain PESs consists of finding the exact solutions to Eq. (2.4). Such a task is key to quantum chemists and, apart from the simplest cases (one-electron systems), is hardly achievable. Thus, one often has to rely on rigorous (but approximate) quantum-mechanical models in order to tackle this issue (Helgaker *et al.* 2000). Once the best (cost-effective) electronic structure method has been selected and applied for a reasonable set of nuclear arrangements, we are frequently faced with the problem of how to accurately represent such huge table of *ab initio* energies. By selecting a reliable analytic model, *e.g.*, a polynomial of the form (Murrell *et al.* 1984)

$$V(\mathbf{R}) = \sum_{a+b+c+\ldots+z=0}^{L} C_{abc\ldots z}\, \hat{\mathcal{S}}\left(\xi_1^a \xi_2^b \xi_3^c \ldots \xi_n^z\right), \tag{2.6}$$

where $C_{abc\ldots z}$ are coefficients, ξ (transformed) internal coordinates and $\hat{\mathcal{S}}$ the operator that ensures permutational symmetry, one is then able to fit such data. Note that, due to the intrinsic errors associated to the truncation of the configuration interaction expansions and incompleteness of the one-electron bases, *ab initio* energies seldom fulfill spectroscopic ($\lesssim 1\,\mathrm{cm}^{-1}$) or even chemical accuracy ($\lesssim 4\,\mathrm{kJ\,mol}^{-1}$) required for dynamics studies. To overcome such difficulties some corrections, like the use of complete basis set extrapolation schemes, must be made prior to the calibration procedure. Furthermore, if spectroscopic accuracy is so desired, additional correlation effects must therefore be envisaged and/or eventually introduce experimental input into the $C_{abc\ldots z}$'s.

3. The link between laboratory astrophysics and PESs

Once a reliable, physically-motivated form for the PES is acquired, an essential step toward spectroscopic and molecular collision attributes involves the solutions to Eq. (2.5); Fig. 1. In studying collision dynamics, whether using Eq. (2.5) or (*quasi-*) classical trajectories (QCT; suitable for collisions involving relatively high kinetic energies and heavier particles), reactive and/or inelastic rate coefficients are the main envisaged outcomes and are obtained by Maxwellian averages of cross sections (Levine 2005). Indeed, for applications in astrophysics, collisional (de-) excitation rates are particularly handy if the PESs entail any of the H, H^+, He or H_2 species as their fragments (Flower 2007). Moreover, in the context of astrochemistry, (thermalized) reaction rate constants and their temperature dependence find their usefulness as input data for gas-phase chemistry networks (Agúndez & Wakelam 2013); the output of which comes normally in the form of molecular abundances. Yet, given its relation to astronomical molecular detection, the calculation of rotation-vibration levels strictly requires accurate solutions to Eq. (2.5). Such a demand also sets high requirements on the quality of the PESs so generated which, for the purposes of spectroscopy (Lodi & Tennyson 2010), are widely appreciated

as (local) quartic force fields. Thus, by employing a convenient body-fixed form for $\hat{\mathcal{T}}_N$ and suitable basis sets in which to expand $|\chi\rangle$, one is then able to compute variationally molecular transition frequencies and, with the knowledge of the dipole moment surfaces and partition functions, Einstein coefficients and line intensities.

4. Case studies: Elemental carbon clusters at the focal point

Recently, we have focused onto the theoretical characterization of PESs of small carbon clusters (C_ns). From an astrophysical viewpoint, these species play a major role in the chemistry of C-stars, comets, and ISM. From the theoretical perspective, elemental C_ns are also appealing as they harbor an intricate chemistry (Varandas & Rocha 2018). For C_3, global PESs of both ground-state singlet [$C_3(1^1A')$, Rocha & Varandas 2018] and lowest triplet [$C_3(1^3A')$, Rocha & Varandas 2019] states have been obtained [using Eq. (2.6) as a general form to represent n-body terms] that accurately fit state-of-the-art *ab initio* energies. With such PESs at hand and Eq. (2.5), ro-vibrational calculations in both ℓ-$C_3(X^1\Sigma_g^+)$ and c-$C_3(^3A_2')$ global minima have been carried out, unveiling an excellent match of the available data on this former (near spectroscopic accuracy for levels up to 9000 cm^{-1} above its ground vibronic state), while assisting with IR band positions for c-$C_3(^3A_2')$ that may serve as guide for its laboratory and astronomical detection. The above PES of $C_3(1^1A')$ and a previously obtained potential for triplet C_4 (Varandas & Rocha 2018) were also utilized as input for the construction of approximate cluster expansions for larger C_ns (n=5–10) (Rocha *et al.* 2019). The global nature of these forms and their notable capability in predicting structural and thermochemical properties of the linear global minima [ℓ-$C_n(^1\Sigma_g^+)$ and ℓ-$C_n(^3\Sigma_g^-)$ for odd- and even-numbered chains, respectively], motivated us to further perform reaction dynamics (QCT) calculations on these PESs. Such studies are on their way and are intended to provide accurate rate coefficients for the neutral-neutral (barrierless) reactions $C_{(n-x)}+C_x \rightarrow C_{(n-y)}+C_y$. We hope that the inclusion of these data into astrochemical models of C-rich circumstellar envelopes and/or interstellar clouds could lead to a refined understanding on the formation of more involved C_ns, PAHs, and their hydrogen deficient precursors.

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