

Theoretical approaches for studying Astrochemistry

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Abstract. The most popular ab initio theoretical approaches that are used to study the gas phase astrochemical reactivity are presented. The methods that are needed for the electronic calculation and the statistical approaches that are used for determining the rate coefficients are detailed.

1. INTRODUCTION

Chemical models are designed to help our understanding of how molecules are synthesized in different regions of the interstellar medium. They consist of a large number of ‘rate equations’ that are differential equations representing how given chemical reactions or physico-chemical processes build-up or lessen the concentration of a particular chemical species. For example, the OSU database osu-09-2008 (http://www.physics.ohio-state.edu/~eric/research_files/osu_09_2008) includes 455 different species connected by 4457 rate equations (the database held at UMIST (www.udfa.net) is very similar). The 455 species include 187 neutral atoms and molecules, 259 atomic and molecular cations, and 6 atomic and molecular anions. In addition, the concentrations of electrons and of neutral and negatively charged grains are included. In time-dependent models, assumptions must be made concerning the starting conditions, the temperature, the elemental abundances and the state (atomic, molecular, ionic) of the elements, and then the differential equations are integrated forward in time to generate molecular abundances at different ages of the cloud. For astrochemical models to be successful all those processes that are important in determining the molecular abundances must be included and the values of the rate coefficients associated need to be close to the correct values. It is the second of these two requirements that is considered in this paper.

The fraction of reactions of astrochemical relevance that have been studied in the laboratory is small. For most of them, rate coefficients have been measured at room temperature and then extrapolated to the temperatures of the interstellar medium to be used in astrochemical models. These extrapolations have often given misleading results. The rate coefficients that have been determined for the conditions of the cold interstellar medium concerns a certain type of reactions; one of the difficulties being the production of normally unstable species (radicals, metastable isomers, ions etc.) that are common in this environment. In such circumstances, a theoretical approach of these processes through what is called computational chemistry is the alternative.

Determining theoretically a rate coefficient is in general a two-step process. The first step focuses on electronic calculations undertaken within the Born Oppenheimer approximation for calculating potential energy surfaces (PES). A PES connect the reactants to the products and can be viewed as a landscape where going one direction or another, represents the geometrical parameters of the molecule in the process of transforming itself from reactants to products and the height of the land, the energy associated with these geometrical parameters. The path along the PES undertaken by the molecule during the

chemical reaction is called the reaction coordinate. Structures for which the energy is minimum, and saddle points (corresponding to transitions states) are among the important features of the PES that need to be determined. In the second step, the PES and other results from the electronic calculations (example: energy balances, dipole moments, polarizabilities, zero point energies) are used to study the motion of the nuclei (collision dynamics). For both steps, methods can range from highly accurate to very approximate.

The most accurate methods for electronic calculations solve the molecular Schrödinger equation associated with the non-relativistic molecular Hamiltonian (for heavy atoms it is however necessary to include relativistic and spin orbit terms). They are known as ab initio methods because they derive directly from first principles, with no inclusion of experimental data. The simplest one is known as the SCF method (Self Consistent Field) and is based on the Hartree–Fock (HF) equations. Since this method approximates the instantaneous electron–electron interactions by an average effect, post Hartree–Fock methods are needed to recover the interaction energy missing because of this approximation (also called the correlation energy). Ab initio methods being widely used for gas-phase astrochemical reactivity, they are developed in section two.

Methods used to study collision dynamics can employ quantum, semi classical and statistical approaches. Since it is essentially statistical methods that are used to calculate rate coefficients for astrochemical models, they are developed in section three.

2. AB INITIO METHODS OF QUANTUM CHEMISTRY

2.1 The Hartree–Fock equations and the SCF method

Since this method is the starting point for any ab initio methods used to study chemical reactivity, the corresponding equations and approximations are set out in the following paragraphs. Post Hartree-Fock methods, which can easily be understood once the Hartree-Fock philosophy is known will only be sketched and references for more reading on the subject are provided for the reader interested in these methods. Some of the textbooks treating the ab initio methods of quantum chemistry at a very accessible level are also given in the list of references.

Quantum Chemistry takes as its starting point the Schrödinger equation $H\Psi = E\Psi$ where H, in atomic units, is a second order differential, N-particle operator:

$$H = \sum_k -1/2\nabla_k^2 + \sum_v (-1/2\nabla_v^2 - \sum_k Z_k/r_{kv}) + \sum_{\mu<v} \sum 1/r_{\mu v} + \sum_{k<l} \sum Z_k Z_l / r_{kl} \quad (1)$$

which covers both the nuclei of indices k and l and the electrons with indices μ and v. The first two terms represent the kinetic energies of the two types of particles, the third the attraction energy of the electrons by nuclei, the last two the repulsion energies between electrons or nuclei. The operator H is a non-relativistic Hamiltonian, ignoring, among others, the coupling between spin moments and orbital moments, which can be introduced at the end of a computation as small perturbations. The Schrödinger equation can only be solved analytically in the case of very simple systems (hydrogen-like atoms, the H_2^+ ion and analogs) but the extension to more complicated structures (di- and poly-atomic molecules) is currently done with good precision through the three following approximations:

- The first one is the Born Oppenheimer approximation that allows for the separation of electronic and nuclear motions. The problem is then reduced to an electronic equation:

$$H_e \Psi_e = E_e \Psi_e \quad (2)$$

$$H_e = \sum_v \left(-1/2\nabla_v^2 - \sum_k Z_k / r_{kv} \right) + \sum_{\mu<v} \sum 1/r_{\mu v} \quad (3)$$

the nuclear repulsion energy $\sum \sum_{k<l} Z_k Z_l / r_{kl}$ is a constant and is added to the electronic energy at each given geometry

- The second approximation considers the electrons as independent particles, which means that an electron is moving in the average field of the others and can be described by a single-electron Schrodinger equation, known as the Hartree Fock equation. This leads to the Self-Consistent field method (SCF). It is a variational method that uses as a starting wave function the initial Slater determinant Φ_e that represents a system with N electron (equation (4)). The method is based on the minimization of the electronic energy E_e calculating the average value of the total Hamiltonian $\langle \Phi_e | H_e | \Phi_e \rangle$, where Φ_e , given the Pauli exclusion principle, is an antisymmetric combination of products of one-electron functions Ψ_i :

$$\Phi_e = 1/(N!)^{1/2} \sum_p \varepsilon_p P_p \psi_1(1) \psi_2(2) \dots \psi_N(N) \quad (4)$$

P_p is a permutation operator that restores the indistinguishability of electrons by changing the position of electrons and ε_p a factor $= \pm 1$ depending on whether the permutation is even or odd so that their fermionic character is respected; ψ , called a spin-orbital, depends only on the space and spin coordinates of a single electron. Usually, the spin-orbital functions ψ are replaced by a product $\varphi(v)\alpha(v)$ or $\varphi(v)\beta(v)$, where $\varphi(v)$ is a function depending only on space coordinates of the electron v . It is multiplied by a discrete function of spin $\alpha(v)$ and $\beta(v)$ according to the direction of spin in the determinant Φ_e . For a system with $2n$ electrons, the electronic energy E_e is minimized with respect to a set of n space orbital φ_i doubly occupied, leading to the introduction of the Fock operator in the calculations:

$$F(v) = H(v) + \sum_{j=1}^n [2J_j(v) - K_j(v)] \quad (5)$$

$H(v)$ is a one-electron operator corresponding to the electron v and J_j and K_j are respectively the Coulomb and exchange operators corresponding to the pair of electrons μ and v assigned to orbitals ϕ_j and ϕ_j in the determinant Φ_e .

In the case of systems with complete shells, we show that orbitals ϕ_i are the solutions of the following equation known as the Hartree-Fock equation. It is soluble numerically in the case of spherically symmetric systems (atoms) or spheroidal systems (diatomic molecules with few electrons).

$$F(v)|\phi_i(v)\rangle = \varepsilon_i |\phi_i(v)\rangle \quad i = 1, \dots, n \quad (6)$$

- the third and last approximation is known as LCAO (for Linear Combination of Atomic Orbitals) that is needed when molecules of arbitrary geometry are treated. Within this approximation, the ϕ_i molecular orbitals are replaced by a linear combination of atomic orbitals:

$$\varphi_i = \sum_{p=1}^m c_{pi} \chi_p \quad m: \text{number of atomic orbitals} \quad (7)$$

where χ_p are atomic orbitals centered on atoms. Determining the functions φ_i is equivalent to determining the coefficients c_{pi} given by a system of integro-differential linear equations: the Roothaan-Hall equations [1, 2]:

$$\sum_{q=1}^m c_{qi} [F_{pq} - \varepsilon_i S_{pq}] = 0, \quad i = 1, \dots, n \quad (8)$$

where c_{qi} and ε_i are the solutions of the secular equation:

$$|F_{pq} - \varepsilon S_{pq}| = 0 \quad (9)$$

The matrix elements involved in this equation can be expressed in terms of atomic orbitals:

$$F_{pq} = H_{pq} + \sum_{j=1}^n (2J_{j,pq} - k_{j,pq}) \quad (10)$$

$$H_{pq} = \langle \chi_p(\mu) | H(\mu) | \chi_q(\mu) \rangle \quad (11)$$

$$S_{pq} = \langle \chi_p(\mu) | \chi_q(\mu) \rangle \quad (12)$$

$$J_{j,pq} = \sum_{r,s=1}^m c_{rj}^* c_{sj} \langle \chi_p(\mu) | \langle \chi_r(\nu) | 1/r_{\mu\nu} | \chi_s(\nu) \rangle | \chi_q(\mu) \rangle \quad (13)$$

$$K_{j,pq} = \sum_{r,s=1}^m c_{rj}^* c_{sj} \langle \chi_p(\mu) | \langle \chi_r(\nu) | 1/r_{\mu\nu} | \chi_q(\mu) \rangle | \chi_s(\nu) \rangle \quad (14)$$

Note that in all these expressions the number of atomic orbitals χ must be assumed at least equal to the number of n occupied molecular orbitals φ : $m \geq n$. When $m > n$, the extra molecular orbitals, φ , not used in the construction of the ground state wavefunction are called virtual orbitals and are used in the post Hartree-Fock approaches.

The Roothaan equations are solved by the following iterative process:

- Calculation of atomic integrals
- Selection of the starting molecular orbital at each step of the iteration cycle
- Construction of the F matrix
- Solving the secular equation which gives the ε_i
- Calculation of the c_{qi} corresponding to the ε_i .

The c_{qi} define a new set of molecular orbitals for a new stage of calculation and so on until convergence, which is obtained when the eigenvectors of the matrix system $|F_{pq} - \varepsilon S_{pq}| = 0$ can reproduce the matrix elements which gave them birth. The total electronic energy of the system is then given by the following formula:

$$E_c = \sum_{i=1}^n (H_{ii} + \varepsilon_i) \text{ with } H_{ii} = \langle \varphi_i(n) | H(n) | \varphi_i(n) \rangle. \quad (15)$$

In the case of a system with an odd number of electrons (called open shells, where the number of electrons of spin α is different from the number of electron spin β) two types of extension of the SCF method described previously are possible:

- either define a Fock operator acting on the doubly occupied orbitals and a Fock operator acting on the single occupied orbitals.
- or define a Fock operator acting on the orbital of α spin and a Fock operator acting on orbitals with a β spin.

In both approaches, we have two systems of coupled integro-differential equations to solve, leading in the first case to the ROHF method [3] and in the second method to the UHF method [4, 5].

As mentioned in the introduction, the major disadvantage of the SCF method is that it is assumed that each electron moves in the average field of the others. It neglects the instantaneous Coulombic interactions between electrons of opposite spin. The correlation between electrons of same spin is instead well described since the SCF wave function is a Slater determinant that respects the Pauli principle. To recover the missing correlation energy Post-Hartree Fock methods are used. They are presented below.

2.2 The Post-Hartree Fock methods

2.2.1 Variational approaches: Configuration interaction methodes

The CI (Configuration Interaction) method is one of the most widely used approaches to the correlation-energy problem. This method is conceptually the simplest even though it raises several computational problems. In this method the wavefunction is given by a linear combination of Slater determinants obtained by exciting the electrons from the SCF molecular orbitals that are occupied in the ground state configuration to the ones that are not occupied (also called virtual) orbitals:

$$\Psi_{\text{CI}} = a_0\Phi_{\text{SCF}} + \sum_S a_s\Phi_s + \sum_D a_D\Phi_D + \sum_T a_T\Phi_T + \dots + \sum_N a_N\Phi_N \quad (16)$$

where the subscript S denotes single excitations, D double excitations, T triple excitations and so on. In the CI calculations, the coefficients are determined variationally by the condition $\delta E/\delta a_k = 0$, the molecular orbitals being taken from the SCF calculation.

If the basis of determinants were complete (full CI) we would obtain exact electronic energies for both ground and excited states of the system by solving the $H_e\Psi_{\text{CI}} = E_{\text{CI}}\Psi_{\text{CI}}$ equation. In practice however, we have to limit the number of excitations (i.e. truncating the CI) for keeping the calculations tractable (the number of determinants grow exponentially with the number of orbitals). This truncation is generally guided by either the nature of correlation effects we want to introduce, or more simply (and more commonly) by limiting the degree of excitations: single excitations (SCI) or single and double excitations (SDCI). Nowadays, it is possible to extend these excitations to triple and/or quadruple in some fashion. The most popular variant is known as the quadratic configuration interaction (QCISD). However, truncated CI suffers from what is called the size consistency problem. Size consistency problems result in the energy of two identical non-interacting molecules (far apart) not being twice the energy of one of them, calculated in the same approximation. This problem worsens as the size of the molecule increases and can be important for example in dissociation energy calculations. A correction has been developed to correct for it, it is known as the Davidson correction [6].

All methods described above use the ground state single SCF determinant as the starting wavefunction. However, in most cases, particularly for bond breaking processes and excited states calculations, this is quite inadequate, and several configurations need to be used for a correct description of the starting wavefunction which is then designed as multiconfigurational:

$$\Psi_{\text{multi}} = \sum_K a_k\Phi_k. \quad (17)$$

In the Multireference self-consistent field method (MCSCF /CASSCF) [7–10] both the a_k coefficients of equation (17) (as in the CI calculations) and the coefficients of the molecular orbitals Φ_k (as in the SCF calculations) are optimized together in the variational process.

When CI calculations are undertaken using a multiconfiguration starting wave function the resulting calculations are designated as Multireference Configuration Interaction (MRCI) [11, 12].

2.2.2 None-variational approaches

Møller–Plesset perturbation methods. Besides the methods of direct configuration interaction, quantum chemistry also uses Møller–Plesset perturbation theory (MP) [13] to recover the electron correlation effects by means of the Rayleigh–Schrödinger perturbation theory (RS-PT). To obtain a perturbation expansion for the correlation energy, the Hamiltonian is partitioned as:

$$H = H_0 + \lambda V \quad (18)$$

where λ is a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation).

H_0 is the Hartree-Fock Hamiltonian,

$$H_0 = \sum_{\nu} F(\nu) = \sum_{\nu} \{H(\nu) + \sum_{j=1}^n [2J_j(\nu) - K_j(\nu)]\} \quad (19)$$

writing

$$v^{\text{HF}}(\nu) = \sum_{j=1}^n [2J_j(\nu) - K_j(\nu)] \quad (20)$$

the perturbation hamiltonian is therefore

$$V = \sum_{\nu < \mu} 1/r_{\nu\mu} - \sum_{\nu} v^{\text{HF}}(\nu). \quad (21)$$

The energy levels and eigenstates of the perturbed Hamiltonian being given by the usual Schrödinger equation

$$(H_0 + \lambda V)\Psi = E\Psi. \quad (22)$$

The energy can then be written as power series in λ

$$E = E_{\text{HF}} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} \dots \quad (23)$$

In most quantum chemistry computer codes, second (MP2) third (MP3) fourth (MP4) and even fifth (MP5) order Møller–Plesset perturbation calculations are possible. However, studies of MP theory have shown that considering higher orders of the perturbation does not necessarily lead to a better converged energy. Indeed, depending on the chemical species and the atomic basis set, the convergence of the MP correction can be rapid or slow, regular, oscillatory or erratic and in the worst case non-existent. Møller–Plesset perturbation calculations are size-consistent.

Here too, it is possible to apply perturbation theory to a multiconfiguration wave function. This leads to approaches referred to as Multireference Perturbation Theory (MRPT/CASPT2) [14–16].

It is possible to combine the configuration interaction and the perturbation approaches within the same treatment of the electronic correlation. This is what is done in the CIPSI method [17].

Coupled Cluster methods. A powerful method, that also overcomes the size consistency problem and that can be considered as an approximation to full CI calculations (even though it is non-variational) exists. It is known as the Coupled Cluster (CC) theory [18–22]. In this theory the exact wave function may be described as a function of an excitation operator T

$$\Psi = e^T |\Phi_{\text{HF}}\rangle \quad \text{with } T = T_1 + T_2 + \dots + T_n. \quad (24)$$

The most commonly used CC approaches in quantum chemical calculations are CCSD (Coupled Cluster Single and Doubles) [23] and CCSD(T) (Coupled Cluster Singles and Doubles with a perturbative treatment of the triple excitations) [24]. Unlike CI calculations in which the terms single and double apply to excitations, in a CC calculation these terms refer to all interactions associated with that quantity of particles (i.e., one and two body interactions). The CCSD(T) method is widely regarded as the most accurate method for calculating ground state potential energy surfaces for the prediction of molecular properties, with respect to both efficiency and accuracy [25, 26]. A Multireference CC (MRCC) method is now available for some quantum chemistry computer codes (<http://www.mrcc.hu>).

2.3 The atomic orbital basis sets

The exact solution of the wave equation for a hydrogenic atom leads to functions, which are products of a radial part $\{\exp(-\zeta.r)\}$ and a spherical harmonic. By extension, the same analytical form has been

used for polyelectronic atoms where the nature of the atom appears in the exponent. They are known as the Slater orbitals. The computational complexity of multicenter integrals between Slater functions has led to use of Gaussian functions. These have the advantage of simplifying the numerical calculations and the disadvantage that we must use a large number to get a correct representation of the electronic distribution. Hence it is necessary to “contract” them to reduce the size of the variational calculations: each of Slater-type function is represented by a linear combination of Gaussian primitives of the form

$$\chi_j = \sum_i c_{ij} e^{-\alpha_i r^2} \quad (25)$$

where the coefficients c and exponents α optimized for the atom, are blocked by groups in the molecular calculations. For good results extensive basis sets need to be used, with atomic orbitals of the free atom represented by many functions in the variational calculation. These leads to basis sets known as double zeta, triple zeta etc. Moreover, for a wave function to describe the electronic system of the molecule uniformly in all regions of space orbitals called “polarization functions” need to be added. Finally, to account for Rydberg states, it is necessary to add diffuse atomic functions. For a correct description of a molecular system, quite extensive atomic basis sets have to be used. The more functions, the greater the degrees of freedom the system has and the energy is better. The disadvantage is that with more basis functions the computational requirements in terms of cpu time and storage increase. Any electronic calculation is defined by the method and the atomic basis set used: for example CCSD/6-311G(d,p) calculations stand for Coupled Cluster single and doubles using a gaussian atomic basis set of triple zeta type (6-311G) extended by polarization functions of d and p type depending of the atom (d,p).

2.4 Accuracy of the ab initio methods

Ab initio electronic structure methods have the advantage that they can in principle be made to converge to the exact solution, when all approximations are sufficiently small in magnitude and when the atomic basis set tends toward the limit of a complete set. In this case full CI tends to the exact non-relativistic solution of the electronic Schrödinger equation. The downside of these methods is their computational cost. They often take enormous amounts of computer time, memory, and disk space. The HF method scales nominally as N^4 (N being the number of basis functions) i.e.: a calculation for a molecule twice as big takes 16 times as long. However in practice it can scale closer to N^3 as the program can identify zero and extremely small integrals and neglect them. Post Hartree-Fock calculations scale even less favorably: MP2 as N^5 , MP4 as N^6 and CCSD(T) as N^7 . However, the problem of computational expense can be alleviated through simplification schemes. For example, in the density fitting scheme, the four-index integrals used to describe the interaction between electron pairs are reduced to simpler two- or three-index integrals, by treating the charge densities they contain in a simplified way. This reduces the scaling with respect to basis set size. Methods employing this scheme are denoted by the prefix “df”. Another scheme is the local approximation, where the molecular orbitals are first localized by a unitary rotation in the orbital space, which leaves the reference wave function invariant, but allows the neglect of interactions from distant pairs of localized orbitals in the correlation calculation. This sharply reduces the scaling of computing time with the molecular size. Methods employing this scheme are denoted by the prefix “L”. Both schemes can be employed together, as in df-LMP2 [27]. Present algorithms in computational chemistry can routinely calculate the properties of molecules that contain up to a few dozen of electrons with high accuracy. Errors for energies can be less than a few kJ/mol. For geometries, bond lengths can be predicted within a few picometers and bond angles within 0.5 degrees.

Let us return to the fundamental approximations of Hartree-Fock theory. All of the methods described above depend on the notion of an effective potential to replace the inter-electronic term in the electronic Hamiltonian. Such a potential is smoothly defined from a mathematical perspective, and it is because of this smoothness that it is fundamentally an unsatisfactory description of the electronic Schrödinger equation. It has been long acknowledged that the true Hamiltonian form displays

singularities in the Coulomb potential at the points where electrons would exist at the same position. To solve what is called the electron cusp problem, methods based on explicitly-correlated wavefunctions have been developed [28, 29]. Such approaches sharply improve the accuracy of ab initio calculations leading to accuracy of less than a kJ/mol. Methods employing this scheme are denoted by the suffix R12 (CCSD(T)-R12) and can be combined with the above “df” “L” schemes (df-LMP2-R12).

The treatment of large molecules (a few hundred of electrons) is computationally tractable using approaches derived from the density functional theory (DFT) [30, 31]. In these approaches, the total energy is expressed in terms of the total one-electron density rather than the wave function, and the solution of the Schrödinger equation is done with an approximate Hamiltonian and an approximate expression for the total electron density. There are difficulties in using density functional theory to properly describe intermolecular interaction especially van der Waals forces (dispersion), charge transfer excitations, transition states, global potential energy surfaces and some other strongly correlated systems. There is therefore some dispute about whether the latter methods are sufficient to describe chemical reactions. They are however considered suitable for structure calculations, for which these methods can be accurate for little computational cost. Presenting these methods is out of the scope of the present paper. A reference for a textbook is however provided for people interested by more reading on the subject.

The reader has to be aware that quantum chemical calculations are not trivial. Even though all methods presented above are implemented in computer codes there is no direct recipe for using them. Whether an SCF or a multiconfiguration starting wave function has to be used, how to recover most of the missing correlation energy, how to describe excited states, how to insure a balanced treatment of the correlation effects all along a potential energy surface, what method is the best for the property studied, all these requirements are molecule dependent and needs the experience and the intuition of the quantum chemist for meaningful results. It is always possible to get numbers from a quantum chemical calculation, but if the physics underlying the chemical problem is not understood and therefore the method used not properly adapted the results will not be correct. Interpretation of the results is not straightforward either and here too the experience of the quantum chemist is needed.

In the present paragraph, we have focused on the electronic methods used to understand chemical reactivity in space. But we must also bear in mind that the same methods can be used for spectroscopic purpose giving quantities that are used directly by observers such as:

- The geometric parameters of a molecule, whose knowledge allows to access to the rotational spectrum of the molecule (in the millimeter wavelength region).
- The dipole moments that allow deduction of the abundance of an emitting species from the intensity of a rotational observed line.
- The molecular vibration frequencies, that give access to the infrared spectrum of the molecule
- The electronic transitions that give access to spectra of the molecule in the ultraviolet range.

3. RATE CONSTANT CALCULATIONS

The rates of chemical reactions are governed by Born-Oppenheimer potential energy surfaces (PES) that can be calculated following the ab initio methods presented above. Once the PES is calculated and fitted to a suitable function form then, in the most accurate quantum dynamics theory, the time-independent or time-dependent Schrödinger equation can in principal be solved for the nuclei by using quantum scattering theory which has been successfully applied to reactive three-atom systems (e.g. reactions between H₂ and F or H). But this approach is still limited to very small systems because of the difficulty of calculating full-dimensional PESs and the large number of quantum states that need to be coupled together for the quantum dynamics. The theory of collisions can be much more simplified if the motion of the nuclei is described by classical mechanics and the motion of the electron quantum mechanically (nuclei moving on a Born-Oppenheimer PES). This approach is known as the Quasi Classical Trajectory (QCT) method. This method has been widely used to study reactive collisions, however, it has its limit

too and it can only be applied when the mass of the nuclei and their collision energy are large compared to those of the electron. For more details on quantum dynamic and QCT methods, the reader is referred to the recent review on theories of reactive scattering [32], which gives all the needed references on both quantum dynamic and QCT methods.

For astrochemical models, a small number of rate coefficients have been determined by the techniques listed above, given the immense computational effort required, and a variety of simpler approaches such as capture theory and statistical approximations have been used for that purpose. It is these approaches that are discussed in this chapter.

3.1 Capture theory

Detailed calculations of reaction rate coefficients require a knowledge of both the long-range and short-range aspects of the intermolecular potentials governing the reactions [33]. However, for exothermic ion-molecule systems especially, it is in general possible to neglect these short-range aspects and to focus on the long-range asymptotic potential.

The orbital angular momentum associated with the relative motion of the reactants under the influence of the long-range potential creates so-called centrifugal barriers. Capture models, in which the sole criterion for reaction is that the reactants must pass over the centrifugal barrier to enter the short-range portion of the potential, can be used [34]. Since some additional dynamical barriers can be created by anisotropies of the potential and short-range effects [28], the capture model provides an upper limit to the actual rate coefficient.

For non-polar neutrals, the long-range potential depends solely on the distance R between ion and neutral, which in many instances is simply the R^{-4} potential arising from the interaction of charge and dipole polarizability. With this potential, the rate coefficient is given by the so-called Langevin expression:

$$k_L = 2\pi e(\alpha_{\text{pola}}/\mu)^{1/2} \quad (26)$$

where e is the electronic charge, α_{pola} is the polarizability, μ is the reduced mass of reactants, and cgs-esu units are utilized so that the units for the rate coefficient are $\text{cm}^3 \text{s}^{-1}$.

For polar neutrals, the potential is anisotropic and depends on the orientation of the permanent dipole (μ_D) as well as the distance between reactants so that it is no longer central in nature. For these cases, astrochemists use in general an approach based on classical trajectory calculations in which the long-range potential as a function of distance and orientation is used [36, 37]. Thermal rate coefficients determined from these calculations can be fitted to analytical expressions depending solely on the reduced mass of the reactants, the polarizability, and the permanent dipole moment of the neutral reactant. This treatment is classical in nature and is only reliable at temperatures above which rotational motion can be considered classical, typically 10–20 K. In this treatment, the best-known formula for the ion-dipolar rate coefficient k_D for linear neutrals is the Su-Chesnavich expression [36]. Maergoiz et al. [37 and reference therein] show that it works reasonably well for neutral species that are linear, symmetric tops, or asymmetric tops. The Su-Chesnavich formula (see for example Maergoiz et al. [37]) is based on the parameter x , defined by

$$x = \mu_D/(2\alpha_{\text{pola}}k_B T)^{1/2} \quad (27)$$

where μ_D is an effective dipole moment of the neutral reactant, which is generally very close to the true dipole moment, and k_B is the Boltzmann constant. The larger the value of x , the larger the rate coefficient is. The expressions for k_D can be written in terms of the Langevin rate coefficient via

$$k_D/k_L = 0.4767x + 0.6200 \quad (28)$$

if $x \geq 2$, and

$$k_D/k_L = (x + 0.5090)^2 / (10.526 + 0.9754) \quad (29)$$

if $x < 2$;

the latter expression reduces to the Langevin expression for $x = 0$.

Alternatively, the expressions can be written in powers of temperature T . For example, for $x \geq 2$

$$k_D = c_1 + c_2 T^{-1/2} \quad (30)$$

where

$$c_1 = 0.62 k_L \quad (31)$$

and

$$c_2 = 2.1179 \mu_D e / (\mu k_B)^{1/2} \quad (32)$$

for $x < 2$, a more complex expression of the type

$$k_D = b_1 + b_2 T^{-1/2} + b_3 T^{-1} \quad (33)$$

pertains, where b_1 is simply the Langevin Rate coefficient, while parameters b_2 and b_3 are given by the expressions :

$$b_2 = 0.4296 \mu_D e / (\mu k_B)^{1/2} \quad (34)$$

and

$$b_3 = \mu_D^2 \pi e / 10.526 k_B (\alpha \mu)^{1/2}. \quad (35)$$

For $x \geq 2$ eq. (30) shows that if the second term is much greater than the first term, which is more likely at low temperatures, the expression reduces to $c_2 T^{-1/2}$ for non-linear neutral reactants. For linear polar neutrals, it is sometimes assumed that the species are rotationally relaxed $J \approx 0$ in which case one can use the so-called ‘‘locked dipole’’ expression [38] which is significantly larger than k_D .

One should note that k_D does not diverge for $T \rightarrow 0$ K as would be suggested by the classical expressions (28) and (30). Instead, k_D levels off at a value $k_D/k_L = (1 + \mu_D / 3 \alpha_{\text{pola}} B)^{1/2}$ where B is the rotational constant (in energy units) of the neutral [37, 39].

As for ion-molecule reactions, a central force potential for structure-less neutral-neutral reactants can be written, and is known as the Lennard-Jones attraction:

$$V(R) = -C_6(R)^{-6} \quad (36)$$

where C_6 can be defined in terms of ionization potentials and polarizabilities of the reactants [40]. The rate coefficient obtained using capture theory with this long-range potential is given after translational thermal averaging, by the equation:

$$k(T) = 8.56 C_6^{1/3} \mu^{-1/2} (k_B T)^{1/6} \quad (37)$$

where all quantities are in cgs units. However, unlike the situation for ion-molecule reactions, this estimate has not received much attention mainly because neutral-neutral reactions involve activation energy. Even for those systems without activation energies, this approximation of k appears to lead to rate constants that are overestimated; moreover, long-range attractions being weak forces, the centrifugal barrier can merge with short-range effects.

3.2 Phase space theory

Capture theories give information neither on the products of reaction if several sets of exoergic products are available nor on the distributions of quantum states of the products. The simplest approach to

these equations for reactions with barrier-less potentials is to make the statistical approximation that all detailed outcomes are equally probable as long as energy and angular momentum are conserved. Such a result requires strong coupling at short range. The most important treatment along these lines is referred as “phase space theory” [41]. In this theory, the cross section σ for a reaction between two species A and B with angular momentum quantum numbers J_A and J_B colliding with asymptotic translational energy E_t to form products C and D in specific vibrational-electronic states with angular momentum quantum numbers J_C and J_D is:

$$\sigma(J_A, J_B \rightarrow J_C, J_D) = \pi \hbar^2 / (2\mu E_t) \times \sum_{L, J} (2L_i + 1) \times P(J_A, J_B, L_i \rightarrow J) \times P'(J \rightarrow J_C, J_D) \quad (38)$$

where J is the total angular momentum number of the combined systems, L_i is the initial relative angular momentum quantum number of reactants, P is the probability that the angular momenta of the reactants add vectorially to form J and P' is the probability that the combined system with angular momentum quantum number J dissociates into the particular final states of C and D, μ is the reduced mass of reactants, and the summation is over the allowable ranges of initial relative angular momentum and total angular momentum quantum numbers.

The probability P' is equal to the sum over L_f , the final relative angular momentum quantum number, of angular momentum allowed ($J \rightarrow L_f, J_C, J_D$) combinations leading to the specific product state divided by the sum of like combinations for all energetically accessible product and reactant states. The ranges of initial and final relative angular momenta are given by appropriate capture models (e.g. Langevin, ion-dipole, Lennard-Jones) as well as angular momentum triangle rules. This procedure involves the implicit assumption that strong coupling among adiabatic centrifugal barriers does not occur at long range. The state- to -state rate coefficient is simply the cross section multiplied by the relative velocity of the two reactants. Summation over all product states, as well as thermal averaging over the reactant state distribution and the translational energy distribution can all be undertaken.

Phase space theory correctly predicts that exothermic reactions occurring on barrier-less potential surfaces proceed on every strong collision. It is also true however that the theory is generally not useful in predicting the branching ratio among several sets of exoergic products because potential surfaces do not often show barrier-less pathways for more than one set of products. The theory is more successful when the potential surfaces involve a deep minimum known as an intermediate complex. In this instance the strong coupling hypothesis comes closest to actuality.

A useful variant of phase space theory if complex lifetimes are needed is based on a unimolecular decay theory of Klots [42]. The reaction is then considered to proceed via a capture cross section to form the intermediate complex which can then dissociate into all available reactant and product states consistent with conservation of energy and angular momentum. The complex dissociation rate $k_{\text{uni}}(\text{s}^{-1})$ into a specific state can be obtained via the principle of microscopic reversibility in terms of the capture cross section of that state, obtained with $P' = 1$ in equation (38) to form the complex. In particular if a complex with angular momentum number J can dissociate into one state of reactants A and B separating with translational energy E_t :

$$k_{\text{uni}} = \rho_{\text{vib}}^{-1} g(J)^{-1} g(J_A) g(J_B) 2\mu E_t \sigma(J_A, J_B \rightarrow J) \quad (39)$$

where ρ_{vib} is the density of complex vibrational states, and g is the rotational degeneracy. A cross section analogous to equation (38) can be formulated in terms of capture to form the complex multiplied by the complex dissociation rate into a particular state divided by the total (summed) dissociation rate. The Klots form for k_{uni} is essentially useful for ion molecule systems where the cross section for complex formation can be assumed to be Langevin or ion-dipole. It is not as useful for neutral-neutral systems where the long range potential is not a good approximation.

3.3 Bimolecular Transition state statistical theory

For most reactions involving neutral neutral molecules (as well as a minority of ion-molecule reactions) short range barriers exist on the PES. The simplest models for taking short-range potential barriers into account, is the “line of center approach” [43] which resembles the capture theories. In this crude approximation it is assumed that structure-less reactants colliding with impact parameter b along a repulsive potential must reach a minimal distance d for reaction to occur. If the potential energy in the absence of angular momentum at d is E_0 , this condition implies that the asymptotic translational energy of reactants E_t must exceed the sum of E_0 and the centrifugal energy $E_t b^2/d^2$ which in turn yields a maximum impact parameter b_{\max} . The thermal averaging over a Maxwell-Boltzmann distribution yields to the following expression for the rate coefficient:

$$k(T) = \pi d^2 (8k_B T / \pi \mu)^{1/2} \exp(-E_0/k_B T). \quad (40)$$

The standard method of including all degrees of freedom is to utilize canonical ensemble statistical mechanics and to imagine that the transition state is in equilibrium with reactants. In the transition state, one of the vibrational degrees of freedom is replaced by the reaction coordinate along which the potential is a maximum (with a corresponding imaginary frequency of vibration). The reaction coordinate is treated as a separable translation, so that the reaction rate coefficient can be envisaged as the equilibrium coefficient between transition state (minus one coordinate) and reactants multiplied by the (averaged) speed of the transition state structure over the saddle point in the potential energy surface. The well-known canonical result for $k(T)$ is given by the formula:

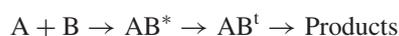
$$k(T) = (k_B T/h) (q_{AB}^\ddagger / q_A q_B) \exp(-E_0/k_B T) \quad (41)$$

for reactants A and B, where E_0 is the energy difference between the transition state and the reactants, referred to as the zero point level, ‡ refers to the transition state and the q are the partition functions per unit volume. The partition functions can be factorized into products representing electronic, vibrational, rotational and translational degrees of freedom.

This formulation for $k(T)$ is known as the activated complex theory or ACT; a more appropriate name would be transition state theory. In the past ACT theory was used mainly to fit transition state characteristics to rate data. Increasingly accurate ab initio calculations of potential energy surfaces now allow purely theoretical and often successful determination of $k(T)$. For more details on the ACT or TST theory the reader is referred to [44].

3.4 Unimolecular transition state theory

Since long-range forces are always attractive, it makes sense to consider theories in which attraction and repulsion occur sequentially. For ion-molecule systems, this is especially important because many potential surfaces are monotonically attractive from long range to formation of a deep minimum at short range but possess transition state barriers in their exit channels which are not large enough to prevent reaction but which affect the reaction dynamics. In addition, there are ion-molecule systems with potential surfaces closer to the norm for neutral-neutral species; in these systems there is only a weak long-range minimum followed by a short-range transition state barrier with energy above that of reactants. For the former type and more arguably for the latter type of potential surface, one can assume that the reaction proceeds through initial formation of a complex, followed by dissociation of the complex back into reactants or over the transition state barrier. If the reactants are labeled A and B, the complex AB^* and the transition state AB^\ddagger , the reaction mechanism is as follows:



which leads to the steady-state rate law

$$d[A]/dt = -k[A][B] \quad (42)$$

$$k = k_{cf}x(k_{cd} + k_{cd'})^{-1}xk_{cd'} \quad (43)$$

where k_{cf} , k_{cd} and $k_{cd'}$ refer to the rates of complex formations, redissociation into reactants, and dissociation into products over the transition state, respectively. One statistical approach to such a system is to use a capture theory for complex formation, to use the Klots formulation of complex redissociation into reactants and to use a third theory for the unimolecular dissociation of the transition complex into products; i.e. the RRKM theory after the four authors Rice, Ramsperger, Kassel, and Marcus. In the RRKM approach, [45] which is analogous to the ACT theory, an equilibrium is envisaged between the activated complex and transition states species. In the microcanonical formulation of RRKM theory, the dissociation rate $k_{RRKM}(s^{-1})$ as a function of (activated) complex total energy E and angular momentum quantum number J is given by the expression:

$$k_{RRKM}(E, J) = N^{\ddagger}[E - E_0 - E_{rot}(J)]/h\rho^*[E - E_{rot}(J)] \quad (44)$$

where N^{\ddagger} refers to the total number of vibrational states of the transition state from its minimum allowable saddle point energy E_0 through E and ρ^* refers to the density of vibrational states of the complex at energy E . For both the transition state and the complex, the available vibrational energy is the total available energy minus the rotational energy $E_{rot}(J)$, which is a function of the angular momentum. That energy not used as vibration or rotation is considered to belong to the separable reaction coordinate.

The role of tunneling in unimolecular reactions grows in importance as the temperature is lowered and hopping over potential becomes more difficult. A one-dimensional tunneling correction to the RRKM expression for the microcanonical unimolecular decay rate coefficient exists [46]. The effective one-dimensional potential representing the reaction coordinate at the saddle point can be assumed to be an Eckart Barrier. The probability of tunneling for each vibrational state of the transition state is computed and this probability takes the place of simply counting the state in the standard formula for k_{RRKM} . In particular, $N^{\ddagger}(E - E_0 - E_{rot})$ in the above equation is replaced by

$$N_{QM}^{\ddagger}(E - E_0 - E_{rot}) = \sum_N P(E - E_0 - E_{rot} - \epsilon_n) \quad (45)$$

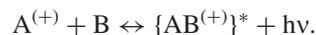
where ϵ_n is the vibrational energy of state n of the transition state with respect to its zero point energy and the sum is over all states n for which the energy in the reaction coordinate (the energy in parenthesis on the right hand side) is negative, but not so negative that the classical energy in the reaction coordinate lies below the minimum of the complex potential well. In general, only few vibrational states of the transition state need to be considered for the tunneling correction.

For reaction mechanisms with more than one potential barrier a combination of capture, ACT, and RRKM approaches can be applied.

3.5 The case of radiative association reactions

In association reactions, two atomic or molecular species, A and B, combine to create a new molecular product, AB. In the ISM, such processes are important, since they allow the growth of species from smaller fragments. Combined products may form having sufficient internal energy to re-dissociate. However, even in dense clouds, the gas density is too low to allow the collisional stabilization of any initially formed adduct. Consequently, the only mechanism by which the adduct can lose energy and generate a stable AB is for it to radiate. The mechanism for radiative association is the same whether or not one of the reactants is charged. The mechanism for polyatomic systems involves the initial formation of an energized complex by the association of the two reactants, followed either by the re-dissociation of the complex or the loss of sufficient energy by the spontaneous emission of radiation so that the complex

then no longer contains sufficient internal energy to re-dissociate; that is



Here the superscript (+) indicates that the reactant A may be neutral or charged. The superscript* indicates that the initially complex will possess sufficient internal energy for $\{AB^{(+)}\}$ to re-dissociate to the reactants $A^{(+)}$ and B. A simple steady-state treatment of this mechanism shows that the second order rate coefficient for radiative association, k_{RA} is given by

$$k_{RA} = k_{ass}\{k_{rad}/(k_{rad} + k_{diss})\}. \quad (46)$$

In this expression, k_{ass} is the second order rate coefficient for the initial formation of $\{AB^{(+)}\}^*$, k_{rad} is the first-order rate coefficient for the radiative stabilization of $\{AB^{(+)}\}^*$ and k_{diss} is the first-order rate coefficient for re-dissociation of the energized complex $\{AB^{(+)}\}^*$ to reactants. Rate coefficient (46) depends on the strength of the $A^{(+)}B$ bond and on the size of the system, that is the number of atoms in the $\{AB^{(+)}\}$ complex. The more atoms, the more vibrations in $\{AB^{(+)}\}$ in which the energy can be distributed, and the slower re-dissociation will be. k_{diss} also depends strongly on the internal energy in $\{AB^{(+)}\}^*$. The above equation for k_{RA} is for a thermal (canonical) system; more detailed microcanonical formulations using phase space theory are also available [47]. For systems in which there is a competitive two-body exit channel, the denominator of (46) must also include a term for adduct dissociation into products. Radiative association can compete with two-body exit channels if (a) there is an exit channel barrier which slows down the product channel, or (b) the potential pathways for association and exothermic reaction are different and do not interact with one another.

For small species, $k_{diss} \gg k_{rad}$ and radiative association is an inefficient process; that is, it occurs in only a small fraction of the collisions in which $\{AB^{(+)}\}^*$ complexes are formed. In these circumstances, k_{RA} simplifies to:

$$k_{RA} = k_{ass}(k_{rad}/k_{diss}). \quad (47)$$

In those cases where only the ground electronic state of the $AB^{(+)}$ species is involved, the radiative process consists of transitions from vibrational levels in $\{AB^{(+)}\}^*$ to vibrational levels in $AB^{(+)}$. The rate of radiative emission in this case can be obtained [48] from the equation:

$$k_{rad} = [1/\rho_s(E)] \sum_{i=1}^{\text{modes}} A_{i,1,0} \sum_{\nu_i=1}^{\nu_{\max}} \eta_i \rho_{s-1}(E - \eta_i h\nu_i) \quad (48)$$

where E is the internal energy in the complex; $\rho_s(E)$ and $\rho_{s-1}(E - \eta_i h\nu_i)$ are the density of states associated with s oscillators at energy E and with s - 1 oscillators at energy $(E - \eta_i h\nu_i)$, the energy $\eta_i h\nu_i$ being 'locked' in the i^{th} oscillator. Values of $A_{i,1,0}$, the Einstein coefficient for spontaneous emission from the $\eta = 1$ to $\eta = 0$ level of the i^{th} oscillator, can be obtained from theory or, in some cases, from experimentally determined infrared absorption coefficients. Values of k_{rad} are generally found to lie within the range $10\text{--}1000 \text{ s}^{-1}$. Because the spontaneous emission coefficients depend on the cube of the emission frequency, higher values of k_{rad} are found for molecules containing hydrogen atoms because they will possess some relatively high vibrational frequencies. One major source of uncertainty in estimating rate coefficients for radiative association arises from the possible role of electronically excited states of $AB^{(+)}$. If such states correlate with $A^{(+)} + B$, then the value of k_{rad} may be dramatically increased. Only ab initio theory can tell if this is the case, and can give the PES of ground and excited states of $AB^{(+)}$ and the electronic transition moments needed for the rate coefficient calculation.

3.6 The case of electronic dissociative recombination reactions

Electronic dissociative recombination (EDR) reactions are processes where a molecular ion recombines with a free electron leading to the fragmentation of the formed complex into two or more fragments.

These processes are very important in space since they contribute to the formation of neutrals from ions and there is a strong need for their rate coefficients and also for their branching ratios. The efficiency of such processes depends on how the various excited electronic states of the complex resulting from the ion-electron recombination interact with the dissociating states leading to fragments. Unless experimental data exist on these processes, it is in general assumed for these barrier-less reactions that the temperature dependence of the rate coefficient goes as $T^{-1/2}$. However, such temperature law dependencies have been shown experimentally to be very crude. Phase space theory has been used to predict the product branching fractions for EDR of polyatomic ions [49] but with a limited success. Indeed, EDR reactions are typically the type of processes for which accurate ab initio calculations and quantum dynamics can hardly be avoided. Although such treatments are rather challenging, the use of quantum theoretical approaches for these processes is in progress. And even if few systems have been studied in this manner; H_3^+ [50], HCO^+ [51] $HCNH^+$ [52] theoretical developments are being undertaken to treat larger systems. Of course, considering the theoretical and computational expenses of such theoretical studies, it is only "key" processes that have to be investigated with these quantum approaches.

Methods presented in this paragraph focuses on the most popular approaches used for determining rate coefficients for astrochemical models. But the field of the collision dynamic is very important for the astrophysical observations. Indeed, none reactive collision rate coefficients can be calculated too. They are very important for the radiative transfer analysis that the astronomers have to undertake to interpret their observations.

4. CONCLUSION

All the methods presented in this paper are the ones most used for gas-phase interstellar chemical reactivity. The species of interest are small enough so that accurate ab initio electronic calculations can be undertaken to provide the PES and other inputs needed to treat the motion of the nuclei using collision dynamics technics. But the reader has to keep in mind that computational and theoretical chemistry can also provide important insights into, and predictions for, chemical systems having thousands of atoms, chemical systems interacting with solid and the solids themselves. This is very important because it is now accepted that among the molecules observed in space some can only be synthesized on grain surfaces. Through which mechanism grains are formed and what is their structure is also an important issue for understanding the interaction of the grains with their environments (example star winds) and their role in star mass loss mechanism.

Before closing the subject, it is important to mention that theoretical developments are always on progress for more realistic and accurate chemical reactivity studies. Among the ones that will benefit astrochemistry, the development that are undertaken in the field of quantum dynamic approaches for larger systems and the ones that are in progress for a better treatment of the chemistry of highly electronically excited states that are crucial for photochemical driven processes.

References

- [1] C.C.C.J. Roothaan, Rev. Mod. Phys., **23**, 69 (1951)
- [2] G.G. Hall, Proc. Roy. Soc., **A205**, 541 (1051)
- [3] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
- [4] G. Berthier, C.R. Acad. Sci., **288**, 91 (1954)
- [5] J. A. Pople, R.K. Nesbet, J. Chem. Phys. **22**, 571 (1954)
- [6] S.R. Langhoff and E.R. Davidson, Int. J. Quantum. Chem. **8**, 61 (1974)
- [7] B. Levy, G. Berthier, Int. J. Quantum Chem. **2**, 307 (1968)
- [8] P. J. Knowles, H.-J. Werner, Chem. Phys. Lett. **115**, 259 (1985)
- [9] B.O. Roos, P.R. Taylor, P.E.M. Siegbahn, Chem. Phys. **48**, 157 (1980)

- [10] B.O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987)
- [11] H.-J. Werner, P.J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988)
- [12] P.J. Knowles, H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).
- [13] C. Møller, M. S. Plesset, *Phys. Rev.* **46**, 618 (1934)
- [14] H.-J. Werner, *Mol. Phys.* **89**, 645 (1996)
- [15] P. Celani, H.-J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
- [16] K. Andersson, P.A. Malmqvist, B.O. Roos, A.J. Sadlej, K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990)
- [17] B. Huron, J-P. Malrieu, P. Rencurel, *J. Chem. Phys.* **58**, 5745 (1973)
- [18] J. Čížek, *J. Chem. Phys.* **45**, 4526 (1966)
- [19] J. Čížek, *Adv. Chem. Phys.* **14**, 35 (1969)
- [20] J. Čížek, J. Paldus, *Int. J. Quantum Chem.* **5**, 359 (1971)
- [21] A. C. Hurley, *Electron Correlation in Small Molecules* (Academic Press, London 1976)
- [22] H. J. Monkhorst, *Int. J. Quantum Chem.* **11**, 421 (1977)
- [23] G. D. Purvis, R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982)
- [24] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- [25] T. J. Helgaker, T. A. Rude, P. Jorgensen, J. Olsen, W. Klopper, *J. Phys. Org. Chem.* **17**, 913 (2004)
- [26] W. Klopper, K. L. Bak, P. Jorgensen, J. Olsen, T. Helgaker, *J. Phys. B: At. Mol. Opt. Phys.* **23**, R103 (1999)
- [27] H.J. Werner, F.R. Manby, P.J. Knowles, *J. Chem. Phys.* **118**: 8149 (2003)
- [28] W. Klopper, *The Encyclopedia of Computational Chemistry*, 2351 (P. V. R. Schleyer, N. L. Allinger, T.Clark, J. Gasteiger, P. A. Kollmann, H. F. Schaefer, P. R. Schreiner, Wiley, Chichester, 1998)
- [29] A. G. Császár, W. D. Allen, Y. Yamaguchi, H. F. Schaefer III, *Computational Molecular Spectroscopy*, 15 (P. R. Bunker and P. Jensen, Wiley, New York, 2000)
- [30] R.G. Parr, W. Yang, *Density-Functionnal Theory of Atoms and Molecules* (New York, Oxford University Press, 1989).
- [31] D. Sholl, J. A. Steckel, *Density Functional Theory: A Practical Introduction* (Wiley-Interscience, 2009).
- [32] W. Hu, G.C. Schartz, *J. Chem. Phys.* **125**, 13230 (2006)
- [33] D.C. Clary, *Rate coefficients in Astrochemistry*, 1 (T.J. Millar, D.A. Williams, Kluwer, Dordrecht, 1988)
- [34] E. Herbst, *Atomic, Molecular and optical Physics handbook*, 429 (G.W.F. Drake 1996)
- [35] J. Troe, *J. Chem. Phys.* **87**, 2773 (1987)
- [36] T. Su, W.J. Chesnavich, *J. Chem. Phys.* **76**, 5183 (1982)
- [37] A.I. Maergoiz, E.E. Nikitin, J. Troe, *Int. J. Mass. Spectro*, **280**, 42 (2009)
- [38] E. Herbst, C.M. Leung, *Astrophys. J.* **310**, 378 (1986)
- [39] J. Troe, *J. Chem. Phys.* **105**, 6249 (1996)
- [40] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954)
- [41] J. Light, *Discussions Faraday Society*, **44**, 14 (1967)
- [42] C.E. Klots, *J. Phys. Chem* **75**, 1526 (1971)
- [43] R.D. Levine, R.B. Bernstein, *Molecular Reaction Dynamics* (Oxford U. Press, 1974)
- [44] I.W.M. Smith: *Kinetics and dynamics of elementary gas reactions* (Butterworths, London 1980)
- [45] K. Holbrook, M. J. Pilling, S. H. Robertson, *Unimolecular Reactions*, (Wiley, 2nd ed. 1996)
- [46] W. H. Miller, *J. Am. Chem. Soc.* **101**, 6810 (1979)
- [47] D.R. Bates, E. Herbst, *Rate coefficients in astrochemistry*, 17 (T.J. Millar and D.A. Williams, Kluwer: Dordrecht, 1988)
- [48] E. Herbst *Chem. Phys.* **65**, 185, (1982)
- [49] E. Herbst, *Astrophys. J.* **222**, 508 (1978)

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- [50] S.F. Dos Santos, V. Kokoouline, C.H. Greene, *J. Chem. Phys.* **127**, 124309 (2007)
- [51] I.A. Mikhailov, V. Kokoouline, A. Larson, S. Tonzani, C.H. Greene, *Phys. Rev. A*, **74**, 032707 (2006)
- [52] A.P. Hickman, R.D. Miles, C. Hayden, D. Talbi, *Ann. Rev. Astron. Astrophys.* **438**, 31 (2005)

Textbooks

- G. Berthier, *Nécessaire de chimie Théorique*, (Ellipse 2009)
- J.L. Rivail, *Eléments de Chimie Quantique à l'usage des chimistes* (EDP interEditions du CNRS Paris 1989)
- A. Szabo, N.S. Ostlund (N.S.) *Modern Quantum Chemistry* (McGraw-Hill, New York, 1982)
- W. Koch, M.C. Holtausen, *A chemist's Guide to Density Functional Theory* (Wiley, Weinheim-Germany 2001)
- Wendell Forst, *Unimolecular Reactions, A concise introduction* (Cambridge University Press, Cambridge 2003)