QUANTUM CHEMICAL MODELLING OF ION-MOLECULE COLLISIONS: A BRIEF OVERVIEW

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Abstract: In the theoretical study of ion-molecule collisions accurate construction of adiabatic potential and non-adiabatic coupling matrix elements plays central role and the accuracy of semi-classical methods (like eikonal method), quantum mechanical methods and simulation techniques like surface hopping dynamics solely depend on the accuracy of the calculated potentials and coupling matrix elements. In this paper we briefly describe various quantum chemical techniques adopted to construct the potential energy surface and coupling matrix elements with high accuracy.

Keywords: adiabatic potential; non-adiabatic coupling matrix elements; quantum chemical

1. Introduction:

The charge transfer process from molecules by ion impact are of great importance in many fields, especially in studies relevant to the planetary atmospheres, the interstellar medium and controlled thermonuclear fusion plasma. In particular, many experimental and only few theoretical investigations are focused on collisions of He^{2+} ion with CO molecule [1-6], since He^{2+} ion is one of the major constituent of the solar wind and CO molecule is commonly found in the comet's neutral atmosphere near the Sun. The interaction of the solar wind with the atmospheres of planets or comets play a crucial role in understanding the X-ray emission from these objects and the interface between the solar wind and their atmospheres. The X-ray emission from charge transfer also has the potential to provide information regarding the composition of the atmospheres and the solar wind.

In the systematic study of the charge transfer process in collisions of ion with molecule, the adiabatic potential energy curves and corresponding coupling matrix elements are to be calculated with considerably high accuracy. Because of the wide variation in the electronic structure of the combined target-projectile system, highly correlated electronic wave functions are needed for the study of ion-molecule interaction.

In this paper a brief summary of theoretical methods used in ion-molecule collisions is given which includes brief discussion on the Hartree-Fock (HF) method, the configuration interaction (CI) method , the self-consistent field (SCF) method and the multireference single- and double-excitation configuration interaction (MRDCI) method.

2. Quantum chemical methods:

The description of the electronic structure of atoms and molecules is one of the important applications of quantum chemistry. The first step is to solve the time-independent Schrödinger equation

$$H\psi(r; R) = E\psi(r; R) \tag{1}$$

with E being the energy eigenvalue and the molecular Hamiltonian in atomic unit [7] is expressed as

$$H = -\frac{1}{2}\sum_{A}\nabla_A^2 - \frac{1}{2}\sum_{i}\nabla_i^2 + \sum_{A}\sum_{B>A}\frac{Z_A Z_B}{R_{AB}} - \sum_{A}\sum_{i}\frac{Z_A}{r_{iA}} + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}} \tag{2}$$

where, A and B refers to nuclei and i and j refers to electrons. The first and the second term in Eqn. (2) are the operators for kinetic energy of the nuclei and of the electrons, respectively. The third term is the potential energy of repulsion between the nuclei, R_{AB} being the internuclear distance between the nuclei A and B with atomic numbers Z_A and Z_B. The fourth term is the potential energy of the attractions between the electrons and

the nuclei, r_{iA} being the distance between the ith electron and nucleus A. The last term is the potential energy of the repulsion between the electrons, r_{ij} being the distance between electrons i and j.

In the Born-Oppenheimer approximation, the nuclei are considered to be at rest as they are much heavier than electrons, so the motion of the nuclei and that of the electrons are decoupled. Accordingly, the wave function for nuclear and electronic motion may be separated, and the electrons will move with respect to the Hamiltonian

$$H_{el} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{iA}} + \sum_j \sum_{i>j} \frac{1}{r_{ij}} + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \tag{3}$$

The Schrödinger equation for electronic motion links the wave function and the energy of the system in its ground or excited state. Using the wave function, all chemical properties can be calculated. The post Hartree-Fock methods are the most developed methods for accurate determination of the many-electron electronic structures of small molecules, especially when the wave function of the system is required to be calculated in the ground state and also in electronically excited states.

3. The Hartree-Fock (HF) method:

The Schrödinger equation cannot be solved exactly for systems containing more than one electron. By introducing some assumptions, however, we can solve it approximately. The complication arises due to the electron-electron repulsion potential term. This term couples electrons together which otherwise try to avoid each other within the presence of the electron-nuclear attraction. The motion of electrons is therefore correlated. The electrons tend to be close to the nuclei and move far apart from eachother, with the result that they can be found most frequently in region near the nuclei. Introducing the one-electron operator f_i and two-electron operator g_{ij}, in the Hamiltonian operator gives

$$H_{el} = \sum_i f_i + \sum_j \sum_{i>j} g_{ij} \tag{4}$$

where

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \; ; \qquad g_{ij} = \frac{1}{r_{ij}} \tag{5}$$

To overcome the problem of the electron-electron repulsion, it can be eliminated in an extreme approximation, resulting in

$$H_{el} \approx \sum_i f_i = H_0 \tag{6}$$

Although it leads to a poor wave function, the advantage is that the Schrödinger equation can be solved exactly, by reducing it to a set of separated one-electron equations,

$$H_0 \Phi_0 = E_0 \Phi_0 \tag{7}$$

where Φ_0 is known as the HF approximation to the exact wave function ψ and it is an antisymmetrized product (Slater determinant) of spin-orbitals, each spin-orbital being a product of a spatial orbital ϕ_i and a spin wave functions, describing the spin of an electron (either up or down). The spatial orbital ϕ_i satisfies the equation

$$f_i(r_i)\phi_i(r_i) = \varepsilon_i \phi_i(r_i) \tag{8}$$

where ε_i is the energy eigenvalue corresponding to the ith electron. In Eqn. (7) the energy eigenvalue E_0 is given as the sum of orbital energies

$$E_0 = \sum_i \varepsilon_i \tag{9}$$

This solution can be improved by considering that an electron is moving in the averaged field of all other electrons. By introducing an approximate electron-electron repulsion term as a one-electron operator $u(r_j)$ in the Hamiltonian

$$H_{el} = \sum_j F(r_j) + \sum_i \sum_{i>j} \frac{1}{r_{ij}} - \sum_j u(r_j) \tag{10}$$

where $F(r_j) = f(r_j) + u(r_j)$ is the Fock operator. It also preserves the separability of the equations

$$F(r_i)\phi_i(r_i) = \varepsilon_i \phi_i(r_i) \tag{11}$$

Since the Fock operator is Hermitian, the eigenfunctions $\phi_i(r_i)$ are orthonormal, or in degenerate cases they can be chosen to be orthonormal. It is required to form a wave function from these orbitals that satisfies the Pauli's exclusion principle and is properly antisymmetric. The energy of the system may be approximated as the first-order perturbation energy. Considering the last two terms of Eqn. (10) as perturbation and expressing it as

$$V = \sum_i \sum_{i>j} \frac{1}{r_{ij}} - \sum_j u(r_j) \tag{12}$$

the energy becomes

$$E = E_0 + \langle \Phi_0 | V | \Phi_0 \rangle \equiv \langle \Phi_0 | H_{el} | \Phi_0 \rangle \tag{13}$$

Minimizing the energy with respect to improving the choice of orbitals while maintaining their orthogonality yields a wave function Φ_0. The set of one-electron eigenvalue Eqn. (7) is solved typically in an iterative way, until self-consistency in the solution is achieved. Employing the variational principle for the energy gives an upper bound to the exact solution, $E \geq E_{exact}$. During the variational procedure, the best form of $u(r_j)$ is also obtained.

4. The configuration interaction (CI) method:

In the configuration interaction (CI) method, one needs an approximate solution of the electronic Schrödinger equation

$$H_{el}\psi(r; R) = E\psi(r; R) \tag{14}$$

where $\psi(r; R)$ can be expressed as a linear combination of Slater determinats built from a complete set of orbitals. This linear combination has infinite terms and its truncation is the foundation of the CI method.

Since electrons also have spin, it is not enough to specify the spatial coordinates of an electron, its spin should also be specified. Therefore, each orbital is considered to be not only a spatial single-particle function ϕ but also a spin function, describing the spin of an electron α (spin-up) and β (spin-down). The orbitals $\psi(r, \omega) = \phi(r)\sigma(\omega)$ are formed accordingly, where r is for position vector of an electron and ω is the coordinate in the spin-space, or we can combine the coordinates into x, hence $\psi(r, \omega) = \psi(x)$. When the coordinates x of two electrons are exchanged, only the sign of the wave function changes

$$\psi(x_1, x_2, x_3, \dots, x_N) = -\psi(x_2, x_1, x_3, \dots, x_N) \tag{15}$$

where $x_1, x_2, x_3, \dots, x_N$ represents the space and spin variables of N electrons. Eqn. (15) also implies that

$$\psi(x_1, x_1, x_3, \dots, x_N) = 0 \tag{16}$$

This enforces the Pauli's exclusion principle, which states that two identical fermions cannot be in the same quantum state simultaneously. In other words, the wave function ψ must be antisymmetric. For two or more electrons, it is not possible to find ψ as a simple product of space and spin functions with this property. One may form a wave function of spin orbitals φ that is properly antisymmetric as

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \dots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \dots & \varphi_N(x_2) \\ \vdots & & \vdots \vdots \vdots & \\ \varphi_1(x_N) & \varphi_2(x_N) & \dots & \varphi_N(x_N) \end{vmatrix}$$

$$\equiv \frac{1}{\sqrt{N!}} \sum_P (-1)^P P |\varphi_1(x_1) \quad \varphi_2(x_2) \quad \dots \quad \varphi_N(x_N)| \tag{17}$$

This is known as Slater determinant [8], where P is a permutation operator and the antisymmetrizer is

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \tag{18}$$

As H_{el} and $\mathcal{A}$ commute, Slater determinants will satisfy Eqns. (7), (8), (9), and (11) for simple products of orbitals. In wave function Φ_0, if one occupied orbital φ_i is replaced, which is occupied by the ith electron by an unoccupied orbital $\varphi_a(a > N)$, which is also eigenfunction of the Fock operator F, then another Slater determinant Φ_i^a is obtained for which

$$F(x_1)\varphi_a(x_1) = \varepsilon_a \varphi_a(x_1) \tag{19}$$
$$H_0\Phi_i^a = E_i^a\Phi_i^a \tag{20}$$

where $E_i^a = E_0 + \varepsilon_a - \varepsilon_i$, is the energy eigenvalue corresponding to Φ_i^a and ε_i is the energy eigenvalue corresponding to φ_i. If only one spin orbital differs, Φ_i^a is described as a single (S) excitation determinant with respect to Φ_0. If two spin orbitals differ it is a double (D) excitation determinant and so on.

Generally, the exact wave function cannot be represented by a single Slater determinant, as it is in the HF approximation. The method is formally a representation of the N-electron Schrödinger wave function on a fixed N-particle sector of Fock space

$$|\psi\rangle = \sum_i c_i |\Phi_i\rangle \tag{21}$$

where $\{\Phi_i\}$ are a suitable complete set of N-electron functions (e.g. Slater determinants) and the c_i are expansion coefficients. The N-electron basis functions $\{\Phi\}$ can form a complete N-body expansion set if they are constructed from a complete (and often orthonormal) single-particle basis set [9]. Such a wave function expansion is known as the full configuration interaction (full CI or FCI) wave function. It is the numerically exact solution of the electronic Schrödinger equation of a many-electron system within the approximation of a given finite single-particle basis set. This is usually the most accurate solution achieved, since the analytical solution is not known.

The correlation effect that two electrons with parallel spin can never occupy the same position in space, called Fermi correlation, is already considered within the HF approximation. Distinct from this is the Coulomb repulsion between electrons with opposite spin, which is usually referred to as the Coulomb correlation. The energy adjustment to HF due to the Coulomb correlation, $E^{FCI} - E^{HF}$ is called the correlation energy [10]. An approximate wave function and also energy to the exact solution can be achieved by a suitable truncation of the FCI expansion, where the energy includes a part of the total correlation energy. As a summary, the relationship between energies at various level of approximations to the exact solution is given as, $E^{HF} > E^{truncated\ CI} > E^{FCI}$.

The exact wave function has additional properties which are in most cases desirable conditions for the approximate wave function. The wave function is an eigenfunction of the spin operator S^2 and S_Z, and that it transforms like an irreducible representation of the molecular point group. A linear combination of Slater determinants fulfilling these conditions is called a 'configuration' [11]. The approximate wave functions obtained using the CI methods are linear combinations of configurations.

To determine the coefficients of the CI expansion the variational method is used [7], in this method, the coefficients are needed that minimize the energy expectation value with respect to the coefficients c_i

$$E = \frac{\langle\psi|H_{el}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{22}$$

The minimum condition $\delta E = 0$ leads to the 'secular' equation

$$\mathcal{H}c = ScE \tag{23}$$

where $\mathcal{H}$ and S are the Hamiltonian and overlap matrices, respectively, whose elements are given by

$$\mathcal{H}_{ij} = \langle\Phi_i|H_{el}|\Phi_j\rangle; \qquad S_{ij} = \langle\Phi_i|\Phi_j\rangle \tag{24}$$

Solving the secular equation (23) gives N values for the energy and N vectors c which, introduced in Eqn. (21), define N approximate molecular wave functions. Choosing the basis set of configurations Φ_i such that it becomes complete when $N \to \infty$ and such that convergance of E is ensured. The 'Hylleraas-Undheim-McDonald theorem' [12, 13] states that the kth lowest eigenvalue of Eqn. (23) is a rigorous upper bound to the kth lowest exact energy, as

$$\mathcal{H}_{ij} = \langle\Phi_i|H_{el}|\Phi_j\rangle = S_{ij} = \langle\Phi_i|\Phi_j\rangle = 0 \tag{25}$$

where Φ_i and Φ_j have different symmetry, it is useful to employ a 'symmetry adapted' basis set such that the secular equation (23) is block diagonal, and can be solved for each block separately. The common procedure is to choose an appropriate (finite) atomic basis set, form linear combinations of Slater determinants which correspond to a given eigenvalue of S^2 and S_Z and transform like a given irreducible representation of the molecular point group, and introduce them in Eqn. (23).

5. The self-consistent field (SCF) method:

In the self-consistent field (SCF) method, a single configuration approach is used and the variational method is applied to determine the orbitals, which defines this configuration [14]. Considering the closed-shell configuration, in which all orbitals are doubly occupied and this configuration has the form

$$\psi = \mathcal{A}|\varphi_1\alpha\varphi_1\beta \quad \dots \quad \varphi_{N/2}\alpha\varphi_{N/2}\beta| \tag{26}$$

which is called the restricted Hartree-Fock (RHF) method. In Eqn. (26) α and β are spin wave functions, with spin quantum numbers $m_s = +1/2$ and $-1/2$, respectively. In the variational method, for small variation $\delta\varphi_i$ the

required condition is, $\delta[\langle\psi|H_{el}|\psi\rangle] = 0$ with the restriction, $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$. Usually, the orbitals φ_i are expressed as a linear combination of a set of n (n > N) basis orbitals, $\{\chi_s\}$

$$|\varphi_i\rangle = \sum_s^n d_{si}|\chi_s\rangle \tag{27}$$

Applying the variational method yields a set of equations with the form of secular equation for the coefficients d_{si}, which defines the canonical orbitals $\{\varphi_i\}$ [15]

$$Fd_i = Sd_iE_i \tag{28}$$

where d_i is a column vector d_{si}, S is the overlap matrix in the $\{\chi_s\}$ basis and F is the matrix of the Fock operator given by

$$F = \langle\chi_s|H_{core}|\chi_t\rangle + \sum_i^{\frac{N}{2}}\sum_{j,k}^n d_{ji}\, d_{ki}\left[2\left\langle\chi_s\chi_j\middle|\frac{1}{r_{12}}\middle|\chi_t\chi_k\right\rangle - \left\langle\chi_s\chi_j\middle|\frac{1}{r_{12}}\middle|\chi_k\chi_t\right\rangle\right] \tag{29}$$

where H_{core} is the kinetic and nuclear attraction operator in the basis $\{\Phi_i\}$. The energy eigenvalue E_i in Eqn. (28) is the energy of the electron described by the orbital φ_i in the average field created by the nuclei and the remainder (N-1) electrons, which occupy the orbitals that define the configuration (26).

For open-shell configurations, the unrestricted Hartree-Fock (UHF) method is usually used, where a treatment similar to that of Eqns. (27), (28) and (29) is applied, but the restriction of the same orbital part for two spin-orbitals of Eqn. (26) is removed. Therefore, a configuration of the following form is used

$$\psi = \mathcal{A}|\varphi_1\alpha \quad \dots\varphi_m\alpha\varphi_{m+1}\beta \quad \dots \quad \varphi_N\beta| \tag{30}$$

6. The MRDCI method:

In the HF approximation, each electron is considered moving in the static electric field of other electrons, hence the correlated motion of electrons (Coulomb correlation) is ignored. The dynamical character of the interactions between electrons may be considered by using CI method. In such sense, electron correlation may be called 'dynamical correlation', which is calculated exactly by using FCI method, or it may be calculated approximately by using truncated CI expansions. Some care is required when the CI expansion is truncated e.g. biradicals or nearly degenerate electronically excited states cannot be correctly described by a truncated single configuration CI wave function.

Two or more Slater determinants in the FCI space may have the same CI expansion coefficients, or coefficients of similar magnitude, due to the (nearly) degenerate molecular orbitals. All of such determinants must be included in the wave function, and treated equally. The electron correlation described by a CI wave function of this kind of determinants is known as 'non-dynamical correlation'. To describe dynamical electron correlation properly in these cases, excitations must be generated 'symmetrically' with respect to either of the equally important determinants [16].

In FCI calculation the computational time to solve the many-body Schrödinger equation increases rapidly with the number of electrons correlated and orbitals included. Many techniques have been developed in quantum chemistry to truncate the FCI expansion with an acceptable loss of accuracy. $|\psi_{FCI}\rangle$ is often written by using some reference configuration function $|\Phi_0\rangle$, and by collecting the many-electron configuration functions based upon their excitation levels relative to $|\Phi_0\rangle$ (singles (S), doubles (D), triples (T), quadruples (Q), and so on), as

$$|\psi_{FCI}\rangle = c_0|\Phi_0\rangle + \sum_{i,a} c_i^a\,|\Phi_i^a\rangle + \sum_{\substack{i<j\\a<b}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k\\a<b<c}} c_{ijk}^{abc}\,|\Phi_{ijk}^{abc}\rangle + .. \tag{31}$$

Inclusion of only the single excitations results in a configuration interaction with singles (CIS) method, which is probably the simplest way to obtain approximations for the excited state energies. Although CIS can provide a description of excited states, it cannot improve the quality of the ground state wave function due to fact that $\langle\Phi_0|H_{el}|\Phi_i^a\rangle = 0$ if the orbitals have been optimized within the HF approach for the ground state wave function. Truncating the expansion (31) by keeping only the single and double excited Φ functions leading to the CISD method

$$|\psi_{CISD}\rangle = c_0|\Phi_0\rangle + \sum_{i,a} c_i^a\,|\Phi_i^a\rangle + \sum_{\substack{i<j\\a<b}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle \tag{32}$$

In a multireference (MR) wave function, also known as multiconfiguration (MC) wave function, only the reference configurations are included in the wave function expansion [16], as

$$|\psi_{MR}\rangle = |\Phi'\rangle + |\Phi''\rangle + |\Phi'''\rangle + \cdots \qquad (33)$$

which allows us to describe both the spin and spatial symmetry of a system properly. Typically, the dynamical electron correlation effect can be considered by all single and double excitations with respect to $|\psi_{MR}\rangle$ by combining Eqns. (32) and (33) to construct a multireference configuration interaction wave function with single- and double-excitation (MRDCI) as

$$|\psi_{MRDCI}\rangle = |\psi'_{CISD}\rangle + |\psi''_{CISD}\rangle + |\psi'''_{CISD}\rangle + \cdots \qquad (34)$$

In considering the possibility of shortening the CI expansion, it is reasonable to discard 'unimportant' configurations from the CI expansion. Configuration selection driven methods, are also called individually selecting CI methods, which are the most appropriate for this purpose. They exploit the fact that the CI Hamiltonian matrix is sparse, only relatively few configurations contributing significantly to the energy or the wave function [17].

In the case of MRDCI, reference configurations can be an arbitrary selection of configurations, commonly selected by their dominance in a CI wave function. This approach has been extensively used in the MRDCI program package [18-25]. In the MRDCI method, the whole MRDCI space is scanned and only those configurations that are found to be important are included in the primary CI expansion. The influence of all other configurations of the MRDCI space on the total energy is obtained by perturbation theory. The use of CI spaces for secular equations which consists of all singly and doubly excited configurations relative to a series of the most important terms in the expansions of desired electronic states [19], fulfills the requirement of providing linear spaces which gives an accurate description of one or more specific eigenfunctions of the Schrödinger equation, and thus to allow for variationally optimized wave functions which are close to the full CI level of accuracy in a suitably flexible atomic orbital (AO) basis. Moreover, the deviations from the full CI limit are corrected using analog to the Davidson-Langhoff correction [26, 27] namely, $\left(1 - \sum_p c_p^2\right)(E_{MRDCI} - E_{ref})$, where E_{MRDCI} is the total energy, E_{ref} is the corresponding energy obtained from the secular equation involving only the reference configurations and c_p is the coefficient of the reference configuration in the CI eigenvector.

7. Summary:

In this paper we have briefly outlined various quantum chemical techniques employed to study the ion-molecule collisions. As in case of ion-molecule collisions there is a wide variation in the electronic structure of the combined target-projectile system, highly correlated electronic wave functions are needed, and hence the multireference single- and double-excitation configuration interaction (MRDCI) approach is preferred over other computationally expensive techniques.

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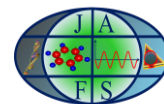
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