

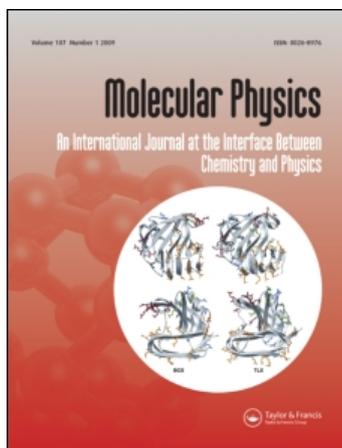
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### Some coherent-states aspects of the electron nuclear dynamics theory: past and present

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## INVITED ARTICLE

### Some coherent-states aspects of the electron nuclear dynamics theory: past and present

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Past and present coherent-states (CS) efforts with the electron nuclear dynamics (END) theory at its simplest level (SL-END) are reviewed. END is a time-dependent, variational, non-adiabatic, direct-dynamics method that describes simultaneously the nuclei and electrons of a molecular system. Within that characterization, SL-END adopts a classical-mechanics description for the nuclei and a quantum single-determinantal representation for the electrons. From its very inception, SL-END has been associated with the CS theory. CS sets are continuous and over-complete sets that satisfy the resolution of identity with a positive measure. Different CS sets can play an astonishing number of roles within SL-END that have several practical consequences. Originally, SL-END utilized the canonical and Thouless CS sets to correctly represent the nuclear and electronic parts of the SL-END wavefunction, respectively, thus defining a proper phase space for the SL-END dynamical equations. Later, canonical and rotational CS sets were used for reconstructing quantum vibrational and quantum rotational descriptions from the SL-END classical nuclear dynamics. That development proved essential to calculate state-resolved properties in ion-molecule and atom-molecule collisions with SL-END. Present CS efforts include a time-dependent Kohn-Sham density-functional-theory direct-dynamic method in the END framework and a CS approach to the charge-equilibration model *inter alia*.

**Keywords:** electron nuclear dynamics theory; coherent-states theory; direct-dynamics method

#### 1. Introduction

The author of this article was a chemistry PhD student in the Quantum Theory Project (QTP), University of Florida, under the supervision of Professor N. Yngve Öhrn and Dr. Erik Deumens from 1991 to 1997, and investigated some coherent-states aspects of the electron nuclear dynamics theory as part of his PhD research. During his time at the QTP, the author also participated in several Sanibel Symposia, both as a *gopher* and as an attendant. Since his graduation, the author has developed other coherent-states aspects and models of the same theory.

The electron nuclear dynamics (END) theory [1–3] by Öhrn and Deumens is indisputably one of the most important contributions in the field of chemical dynamics originated in the QTP. It is challenging to elucidate END in a few words and no explanation on my part can substitute the enlightening reviews written by the END creators [1–3]. Nevertheless, one can capture most of the essence of END by drawing attention to its direct-dynamics nature. Direct-dynamics methods [4–8] are those where the forces acting among the reaction participants are calculated ‘on the fly’, as the reaction simulation proceeds. Such an approach avoids the

cumbersome predetermination of complete potential energy surfaces (PES), as is the case for more traditional approaches to dynamics. In a sense, a direct-dynamics simulation replicates the spontaneity of a chemical reaction by progressing without the intermediation of pre-calculated PES. Although END was not the first direct-dynamics method ever conceived [4–8], it stands out from its predecessors by its unique attributes. In that regard, END is a time-dependent, variational, non-adiabatic, direct-dynamics method that describes simultaneously the nuclei and electrons of a molecular system. END starts by prescribing a trial total wavefunction  $|\Psi_{\text{END}}\rangle$  for both the nuclear and electronic degrees of freedom. Then, the END dynamical equations are obtained by applying the time-dependent variational principle (TDVP) [9] to  $|\Psi_{\text{END}}\rangle$ . That procedure involves the quantum action  $A_{\text{END}}$

$$A_{\text{END}}[\Psi_{\text{END}}^*, \Psi_{\text{END}}] = \int_{t_1}^{t_2} dt L_{\text{END}}[\Psi_{\text{END}}^*, \Psi_{\text{END}}] \quad (1)$$

with quantum Lagrangian  $L_{\text{END}}$

$$L_{\text{END}}[\Psi_{\text{END}}^*, \Psi_{\text{END}}] = \langle \Psi_{\text{END}} | i \frac{\partial}{\partial t} - \hat{H}_{\text{Total}} | \Psi_{\text{END}} \rangle \times \langle \Psi_{\text{END}} | \Psi_{\text{END}} \rangle^{-1} \quad (2)$$

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where  $\hat{H}_{Total}$  is the total Hamiltonian. Following the TDVP [9], the END dynamical equations are obtained by imposing the stationary condition onto  $A_{END}$

$$\delta A_{END}[\Psi_{END}^*, \Psi_{END}] = \delta \int_{t_1}^{t_2} dt L_{END}[\Psi_{END}^*, \Psi_{END}] = 0 \quad (3)$$

with the boundary conditions  $\delta|\Psi_{END}(t_1)\rangle = \delta|\Psi_{END}(t_2)\rangle = 0$  at the endpoints. Equation (3) leads to a set of Euler–Lagrange equations for the variational parameters of  $|\Psi_{END}\rangle$  that determine  $|\Psi_{END}\rangle$ 's time evolution. Within the above characterization, END is conceived not as one model, but as a hierarchy of related models ordered by the level of sophistication of the nuclear and electronic descriptions imparted on  $|\Psi_{END}\rangle$  [3]. The END models are formulated by adapting various electronic structure methodologies (e.g. the Hartree–Fock (HF) [1,10] and the multi-configuration self-consistent field [10,11] methods) into the nuclear and the electronic parts of  $|\Psi_{END}\rangle$ . The implied extension of electronic-structure methods to nuclei via wavefunctions with nuclear molecular orbitals is akin to contemporaneous efforts in the time-independent realm [12,13]. From its base, the END hierarchy starts with the simplest-level END (SL-END) [1–3]. SL-END adopts a trial total wavefunction  $|\Psi_{SL-END}\rangle = |\Psi_N\rangle|\Psi_e\rangle$ , where the nuclear wavefunction  $|\Psi_N\rangle$  is a product of frozen, narrow-width, Gaussian wave packets, and the electronic wavefunction  $|\Psi_e\rangle$  is a single-determinantal state.  $|\Psi_N\rangle$  is actually used in the zero limit of the wave packets widths so that  $|\Psi_N\rangle$  provides a classical-mechanics description for the nuclei. Due to suitable parameterizations in  $|\Psi_N\rangle$  and  $|\Psi_e\rangle$ , the SL-END dynamical equations exhibit a generalized symplectic form [9] that resembles the classical Hamilton equations [14] (see Section 2.1). Despite its deceiving simplicity, SL-END can appropriately describe a wealth of chemical phenomena. In fact, SL-END is the most utilized version of END and has proven accurate for the simulation of proton-molecule ( $H^+ + H_2$  [15,16],  $H^+ + CH_4$  [17],  $H^+ + H_2O$  [18],  $H^+ + C_2H_2$  [19,20],  $H^+ + HF$  [21],  $H^+ + CF_4$  [22]), hydrogen-molecule ( $H + D_2$  [23],  $H + HOD$  [24]), and molecule-molecule ( $D_2 + NH_3^+$  [25]) reactions, and intramolecular processes [26] *inter alia*.

END is a wide-ranging methodology that has efficiently combined various theoretical and computational features into its structure. Therefore, there are numerous aspects of END that can motivate enlightening commentaries and further developments. Out of many possible aspects, this article will only examine past and present coherent-states (CS) [27] efforts

with SL-END. The concentration on SL-END alone is certainly justified by its predominance and adequacy to describe chemical processes, as discussed previously. However, the CS theory is also relevant for the higher-level versions of END (e.g. the vector CS formulation of the multi-configurational END [10]), but those more advanced developments will not be considered here. A complete account of the CS theory within the SL-END context is given in Section 2.2. However, at this point, it suffices to know that CS are sets of functions that (1) are continuous with respect to some parameters and (2) satisfy the resolution of identity with an appropriate measure, which in most cases is positive [27]. Due to those properties and others, the CS sets form continuous and over-complete basis sets in contrast to the discrete and (in principle) complete basis sets usually employed in quantum chemistry. Within the provided definition, various types of CS sets have been formulated, and the reader is referred to the book by Klauder and Skagerstam [27] for a complete survey of the different CS sets. However, for SL-END, three CS sets turn out to be relevant: (1) The canonical CS set [27] associated with the harmonic oscillator Hamiltonian, (2) a rotational CS set [28] associated with the rotational Hamiltonian, and (3) the Thouless CS set [27] associated with electronic single-determinantal states (e.g.  $|\Psi_e\rangle$  of SL-END); those CS sets are explained in detail in Section 2.2. In the context of SL-END, those CS sets can play three important roles: (1) when used to represent the SL-END wavefunction  $|\Psi_{SL-END}\rangle$ , the canonical and Thouless CS sets furnish their CS parameters as the  $|\Psi_{SL-END}\rangle$  variational parameters that define an adequate phase space for the SL-END dynamical equations via the TDVP [1–3], (2) when used to analyse the SL-END wavefunction  $|\Psi_{SL-END}\rangle$ , the canonical and the rotational CS sets permit reconstructing some degree of quantum description from the SL-END classical nuclear dynamics [15,16,28] (that procedure provides quantum vibrational and quantum rotational transition probabilities for state-resolved properties), (3) when used as continuous and over-complete sets, the three CS sets permit deriving the SL-END dynamical equations from a CS path-integral representation of the propagator [27]. This last aspect is important to bring about fruitful interactions between SL-END and semiclassical approaches that utilize the canonical CS set to represent the propagator [29,30]. The three roles of the CS sets in SL-END will be discussed in Section 2 (Roles 1 and 2) and in Section 3 (Role 3).

The CS theory has a long history in physics and has found a vast array of applications in mathematical physics, condensed matter theory, atomic physics,

nuclear physics, and quantum field theory [27]. In theoretical chemistry, the use of CS sets is more recent and restricted; however, in view of some aspects to be discussed here, the CS theory has a promising future in that field. END has made several important contributions concerning the utilization of CS sets in theoretical chemistry. However, END is not the only method that employs CS in that field and has taken inspiration from earlier CS efforts. For instance, the SL-END use of canonical CS as the wave packets in  $|\Psi_N\rangle$  has a precedent in the semiclassical wave packets dynamics of Heller [31]. The use of the canonical CS set to reconstruct some quantum vibrational description from classical dynamics was pioneered by the DECENT method of Gentry and Giese [32]. The rotational CS [28] used for reconstructing some quantum rotational description from classical dynamics followed from an earlier rotational CS set developed by Janssen [33]. The Thouless CS set found many applications in nuclear physics (e.g. to determine the stability of the HF equations, to formulate nuclear dynamics, etc.) [34], which were later extended to analogous electronic-structure problems. As mentioned earlier, the canonical CS path-integral representation of the propagator was utilized in the context of the semiclassical theory by Herman and Kluk [29] and by Miller [30]. However, despite all the mentioned predecessors, the CS aspects of SL-END exhibit a high level of originality because of two main features. First, SL-END utilizes several types of CS sets – some preexisting (canonical and Thouless CS sets) and some originally formulated (rotational CS set [28] and recent developments [35] – for all the types of particles in a molecular system (nuclei and electrons) and for all types of degrees of freedom (translational, rotational, vibrational and electronic). In contrast, all previous CS efforts in theoretical chemistry utilized only one type of CS set at a time, in most cases being the ordinary canonical CS set [29,30]. Second, SL-END utilizes the previous CS sets within its advanced direct-dynamics framework. In contrast, most previous CS efforts in theoretical chemistry utilized CS sets in conjunction with pre-calculated or model PES [31].

This article is organized as follows. In Section 2, some past CS efforts with the SL-END theory developed by the author as a PhD student will be reviewed [15–18,28,36]. That survey includes a brief discussion of the SL-END theory itself (Section 2.1), a detailed discussion of the CS sets relevant for SL-END (Section 2.2), and a detailed discussion of the use of those CS sets for SL-END simulations (Section 2.3). In Section 3, some present CS efforts with the SL-END theory under current development in the author's

research group will be reviewed. Those efforts include a time-dependent density-functional-theory direct-dynamics method in the SL-END framework [37], a novel CS approach [35] to charge-equilibration models via the valence-bond theory [10], and a CS path-integral approach to SL-END *inter alia* [20–22].

## 2. Past CS Efforts with the SL-END Theory

### 2.1. The SL-END theory

For the sake of clarity, it is convenient to discuss first the SL-END theory without reference to the CS theory. With SL-END so explained, it will be easier to analyze its subsequent CS aspects in Section 2.2. As discussed before, SL-END [1–3] adopts a classical-mechanics description for the nuclei and a quantum single-determinantal representation for the electrons. Having a molecular system with  $N_N$  nuclei and  $N_e$  electrons, and with total Hamiltonian  $\hat{H}_{Total}$ , the SL-END total trial wavefunction  $|\Psi_{SL-END}\rangle$  is the product of a nuclear  $|\Psi_N\rangle$  and an electronic  $|\Psi_e\rangle$  wavefunction:  $|\Psi_{SL-END}\rangle = |\Psi_N\rangle|\Psi_e\rangle$  is the product of  $3N_N$  frozen, narrow-width, 1-D Gaussian wave packets:

$$|\Psi_N\rangle = |\mathbf{R}, \mathbf{P}\rangle = \prod_{i=1}^{3N_N} |R_i P_i\rangle = \prod_{i=1}^{3N_N} \exp \left[ -\left( \frac{X_i - R_i}{2\Delta R_i} \right)^2 + iP_i(X_i - R_i) \right] \quad (4)$$

with average positions  $R_i$ , average conjugate momenta  $P_i$ , and widths  $\Delta R_i$ ;  $R_i$  and  $P_i$  are the variational parameters of  $|\Psi_N\rangle = |\mathbf{R}, \mathbf{P}\rangle \cdot |\Psi_N\rangle$  will be treated under the TDVP in the limit of zero widths  $\Delta R_i$ ; under those conditions,  $|\Psi_N\rangle$  renders a nuclear classical dynamics in terms of the positions and momenta  $\{R_i(t), P_i(t)\}$  [1–3,14] [cf. Equation (9)]. The electronic wavefunction  $|\Psi_e\rangle$  is a single-determinantal state  $|\mathbf{z}, \mathbf{R}\rangle$  in the Thouless representation [38]. To construct that state,  $K$  creation and annihilation operators  $b_i^\dagger$  and  $b_i$  of  $N_e$  occupied  $\{\psi_h = \phi_{h\sigma}\sigma\}$  and  $K - N_e$  virtual  $\{\psi_p = \phi_{p\sigma}\sigma\}$  orthonormal molecular spin-orbitals (MSO) are considered. Taking  $|0\rangle = b_{N_e}^\dagger \dots b_1^\dagger |\text{vac}\rangle$  as a reference, the Thouless single-determinantal state  $|\Psi_e\rangle = |\mathbf{z}, \mathbf{R}\rangle$  is [38]:

$$|\Psi_e\rangle = |\mathbf{z}, \mathbf{R}\rangle = \det(\chi_h) = \exp \left( \sum_{p=N_e+1}^K \sum_{h=1}^{N_e} z_{ph} b_p^\dagger b_h \right) |0\rangle; \quad (5)$$

$$\chi_h = \psi_h + \sum_{p=N_e+1}^K z_{ph} \psi_p \quad (1 \leq h \leq N_e)$$

where  $\{\chi_h\}$  are the dynamical spin-orbitals (DSO) [1,38] in terms of the complex-valued Thouless

parameters  $\{z_{ph}\}$ . Those parameters and the nuclear positions  $\{R_i\}$  are the variational parameters of  $|\Psi_e\rangle = |\mathbf{z}, \mathbf{R}\rangle$ . The MSO  $\{\psi_i\} = \{\psi_h, \psi_p\}$  used for  $|\mathbf{z}, \mathbf{R}\rangle$  are of a HF type, obtained from the standard time-independent HF equations. The HF MSO are constructed with standard atomic basis set functions centred on the moving nuclear wave packets. For that reason, the HF MSO, DSO, and  $|\mathbf{z}, \mathbf{R}\rangle$  depend upon the nuclear positions  $\{R_i\}$ . The HF MSO and DSO are unrestricted with respect to spin so that  $|\mathbf{z}, \mathbf{R}\rangle$  can properly describe bond-breaking and bond-forming processes, at least qualitatively. While the HF MSO are fully orthogonal, the DSO are non-orthogonal within spin blocks as can be seen from Equation (5).

The Thouless representation of a single-determinantal state has been profusely applied in nuclear physics [34], and END has further extended its use to chemical dynamics. The advantages of utilizing a non-standard Thouless single-determinantal state in TDVP treatments is summarized below, but more detailed discussions can be found in Ref. [1–3,9,34]. The Thouless representation permits expressing all the single-determinantal states  $|\mathbf{z}, \mathbf{R}\rangle$  from a reference  $|0\rangle$  that are non-orthogonal to  $|0\rangle$  in terms of a minimum number of continuous and complex-valued parameters  $\{z_{ph}\}$  with a given basis set of rank  $K$  [34]. Those minimum-number or non-redundant parameters  $\{z_{ph}\}$  provide a one-to-one mapping between them and the non-equivalent states  $|\mathbf{z}, \mathbf{R}\rangle$  up to a normalization constant and global phase factor. Therefore, the Thouless representation allows an unequivocal sampling of all the non-equivalent single-determinantal states from  $|0\rangle$  during a variational procedure. If those single-determinantal states were parameterized in terms of the atomic coefficients of their MSO, there would not be a one-to-one mapping between those coefficients and the states because the former can be changed by unitary transformations among occupied MSO while the state remains unchanged. That invariance indicates that the MSO atomic coefficients are redundant parameters to express single-determinantal states. Redundant parameters not only preclude a one-to-one mapping that distinguish non-equivalent states but also lead to numerical instabilities during dynamics [1]. Those instabilities are avoided by the Thouless representation through its non-redundant parameterization. Moreover, the continuous and complex-valued Thouless parameters permit expressing the electronic dynamics in terms of pairs of generalized conjugate variables  $\{z_{ph}(t), z_{ph}^*(t)\}$  [1–3,9] that play an analogous role to that of the nuclear conjugate variables  $\{R_i(t), P_i(t)\}$  [14] (See below).

The SL-END dynamical equations are obtained by subjecting the trial wavefunction  $|\Psi_{\text{SL-END}}\rangle$  to the

TDVP [1–3,9] with respect to its variational parameters  $\{R_i(t), P_i(t), z_{ph}(t), z_{ph}^*(t)\}$  (cf. Equations (1) and (2)). The quantum Lagrangian  $L_{\text{SL-END}}$ , Equation (2), involving the SL-END wavefunction  $|\Psi_{\text{SL-END}}\rangle$  is in the limit of zero widths  $\Delta R_i$  of  $|\Psi_N\rangle$  (cf. Ref. [2])

$$L_{\text{SL-END}}[\mathbf{R}, \mathbf{P}, \mathbf{z}, \mathbf{z}^*] = \sum_{j=1}^{3N_N} \left[ P_j + \frac{i}{2} \left( \frac{\partial \ln S}{\partial R_j} - \frac{\partial \ln S}{\partial R_j'} \right) \right] \dot{R}_j + \frac{i}{2} \sum_{p,h}^{K-N_e, N_e} \left( \frac{\partial \ln S}{\partial z_{ph}} \dot{z}_{ph} - \frac{\partial \ln S}{\partial z_{ph}^*} \dot{z}_{ph}^* \right) - E_{\text{Total}}[\mathbf{R}, \mathbf{P}, \mathbf{z}, \mathbf{z}^*] \quad (6)$$

where  $E_{\text{Total}}$  is the total energy, and  $S = \langle \mathbf{z}', \mathbf{R}' | \mathbf{z}, \mathbf{R} \rangle$ . The former is

$$E_{\text{Total}} = \langle \Psi_{\text{SL-END}} | \hat{H}_{\text{Total}} | \Psi_{\text{SL-END}} \rangle / \langle \Psi_{\text{SL-END}} | \Psi_{\text{SL-END}} \rangle = \sum_{i=1}^{N_N} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i=1, j>i}^{N_N} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + E_e[\mathbf{R}, \mathbf{z}, \mathbf{z}^*] \quad (7)$$

where the first and second terms in the last line are the classical nuclear kinetic and nuclear repulsive energies, respectively, and  $E_e$  is the electronic energy. Following TDVP, the stationary condition on the quantum action  $A_{\text{SL-END}}[\mathbf{R}, \mathbf{P}, \mathbf{z}, \mathbf{z}^*]$  with the usual boundary conditions renders the SL-END dynamical equations as a set of Euler-Lagrange equations for the variational parameters  $\{\zeta_i(t)\} = \{R_i(t), P_i(t), z_{ph}(t), z_{ph}^*(t)\}$  [1–3,9]

$$\frac{\partial L_{\text{SL-END}}}{\partial \zeta_i} - \frac{d}{dt} \left( \frac{\partial L_{\text{SL-END}}}{\partial \dot{\zeta}_i} \right) = 0 \quad (8)$$

that in matrix form is

$$\begin{bmatrix} i\mathbf{C} & \mathbf{0} & i\mathbf{C}_{\mathbf{R}} & \mathbf{0} \\ \mathbf{0} & -i\mathbf{C}^* & -i\mathbf{C}_{\mathbf{R}}^* & \mathbf{0} \\ i\mathbf{C}_{\mathbf{R}}^\dagger & -i\mathbf{C}_{\mathbf{R}}^T & \mathbf{C}_{\mathbf{RR}} & -\mathbf{I} \\ \mathbf{0} & \mathbf{0} & \mathbf{I} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \frac{d\mathbf{z}}{dt} \\ \frac{d\mathbf{z}^*}{dt} \\ \frac{d\mathbf{R}}{dt} \\ \frac{d\mathbf{P}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial E_{\text{Total}}}{\partial \mathbf{z}^*} \\ \frac{\partial E_{\text{Total}}}{\partial \mathbf{z}} \\ \frac{\partial E_{\text{Total}}}{\partial \mathbf{R}} \\ \frac{\partial E_{\text{Total}}}{\partial \mathbf{P}} \end{bmatrix} \quad (9)$$

with dynamic metric matrices:

$$\begin{aligned} (\mathbf{C}_{XY})_{ik,jl} &= -2\text{Im} \frac{\partial^2 \ln S}{\partial X_{ik} \partial Y_{jl}} \Big|_{\mathbf{R}'=\mathbf{R}}; \\ (\mathbf{C}_{X_{ik}})_{ph} &= \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial X_{ik}} \Big|_{\mathbf{R}'=\mathbf{R}}; \\ \mathbf{C}_{ph,qg} &= \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial z_{qg}} \Big|_{\mathbf{R}'=\mathbf{R}} \end{aligned} \quad (10)$$

Equation (9) is a quantum generalization of the classical Hamilton equations in symplectic notation [9,14]. More precisely, Equation (9) expresses the coupled nuclear classical dynamics and electronic quantum dynamics in a generalized symplectic notation [9,14] via the pairs of conjugate variables  $\{R_i(t), P_i(t)\}$ , and  $\{z_{ph}(t), z_{ph}^*(t)\}$  of the wavefunction phase space [2,9].

In a SL-END simulation, the reactants are prepared in the initial electronic state  $|\mathbf{z}^{(i)}, \mathbf{R}^{(i)}\rangle$  with initial positions and momenta  $\{R_i^{(i)}\}$  and  $\{P_i^{(i)}\}$  that define the initial total wavefunction  $|\Psi_{\text{SL-END}}^{(i)}\rangle$ . The initial Thouless parameters can be taken as  $\mathbf{z}^{(i)} = \mathbf{0}$  so that  $|\mathbf{z}^{(i)} = \mathbf{0}, \mathbf{R}^{(i)}\rangle = |0\rangle$  (cf. Equation (5)). That reference  $|0\rangle$  is a standard HF single-determinantal state constructed with orthogonal HF MSO  $\{\psi_h\}$  that satisfy the time-independent HF equation. As the simulation proceeds according to Equation (9), the parameters  $\{z_{ph}(t)\}$  will become non-zero and the single-determinant state  $|\mathbf{z}, \mathbf{R}\rangle$  will take its general form, Equation (5). In the end, the final parameters  $\{R_i^{(f)}, P_i^{(f)}, z_{ph}^{(f)}$  and  $z_{ph}^{(f)*}\}$  determine the final total wavefunction  $|\Psi_{\text{SL-END}}^{(f)}\rangle$  from which several reaction properties can be obtained (e.g. products prediction, energy transfers, differential and integral cross sections, etc.).

## 2.2. The CS sets relevant for the SL-END theory

Having reviewed SL-END, a discussion of the CS theory can be presented. The most accepted definition of CS has been given by Klauder [27]: A set of states  $\{|\zeta_i\rangle\}$  in a Hilbert space that depend on a set of parameters  $\{\zeta_i\}$  form a CS set if those states satisfy two conditions: (1) The continuity condition, *i.e.*, the states  $\{|\zeta_i\rangle\}$  are continuous with respect to their parameters  $\{\zeta_i\}$ ; and (2) the resolution of identity condition,  $1 = \int d\mu(\zeta_i) |\zeta_i\rangle \langle \zeta_i|$ , with a positive measure  $d\mu(\zeta_i) > 0$ . In some CS sets [28,33], the second condition adopts a weaker formulation [27] whereby the resolution of identity can be achieved with an indefinite measure (*i.e.*  $d\mu(\zeta_i)$  can be positive or negative with different values of its arguments  $\{\zeta_i\}$ ). Since the CS sets are usually non-orthogonal ( $\langle \zeta_i | \zeta_i' \rangle \neq 0$ ), the two CS conditions imply that the CS form a continuous and over-complete set [27]. Various types of CS sets have been formulated within the previous definition [27], but only those relevant to SL-END will be discussed here.

From its inception, SL-END has included two types of CS sets in its formalism [1]. First, each Gaussian wave packet  $\{|R_i, P_i\rangle\}$  in  $|\Psi_N\rangle$ , Equation(4), is a (un-normalized) member of a canonical CS set expressed with real CS parameters  $\{\zeta_i\} = \{R_i, P_i\}$  [27].

The canonical CS set admits an equivalent complex parameterization:  $\{|Z_i\rangle, Z_i = \sqrt{m_i \omega_i / 2} R_i + i \sqrt{1/2m_i \omega_i} P_i\}$ , where the masses  $m_i$  and angular frequencies  $\omega_i$  are those of 1-D harmonic oscillator Hamiltonians  $\hat{H}_{HO}$  (See next paragraph for more details). The canonical CS set has a positive measure that in its complex parameterization is  $d\mu(Z_i) = \frac{1}{\pi} d\text{Re}Z_i d\text{Im}Z_i$  [27]. Second, the Thouless single-determinantal state  $|\mathbf{z}, \mathbf{R}\rangle$ , Equation (5), is a (un-normalized) member of the Thouless CS set [27]:  $\{|\mathbf{z}\rangle\}$  with complex CS parameters  $\{\zeta_i\} = \{z_{ph}\}$ . The Thouless CS set admits an equivalent real parameterization, somewhat analogous to the  $R_i - P_i$  parameterization of the canonical CS set, which need not be considered further in the present context. The Thouless CS set has a positive measure whose expression is given in Ref. [27]. The canonical and Thouless CS sets are explicitly associated with SL-END [1]. However, a third and non-obvious rotational CS set [28] should be brought to the SL-END formalism to complete its dynamical description as discussed below.

Some CS sets satisfy additional conditions to those in the CS definition [27]. However, only the quasi-classical condition [39] is relevant here. Taking as an example a generic and normalized CS set  $\{|q_i, p_i\rangle\}$  with a real  $q_i - p_i$  parameterization, that set is quasi-classical with respect to a Hamiltonian  $\hat{H}$  if the CS average positions  $\langle \hat{x}_i \rangle = \langle q_i(t), p_i(t) | \hat{x}_i | q_i(t), p_i(t) \rangle = q_i(t)$  and momenta  $\langle \hat{p}_i \rangle = \langle q_i(t), p_i(t) | \hat{p}_i | q_i(t), p_i(t) \rangle = p_i(t)$  evolve in time with  $\hat{H}$  according to the classical Hamilton equations:  $\dot{q}_i = \partial H(q_i, p_i) / \partial p_i$  and  $\dot{p}_i = -\partial H(q_i, p_i) / \partial q_i$ , where  $H(q_i, p_i) = \langle q_i(t), p_i(t) | \hat{H} | q_i(t), p_i(t) \rangle$ . For instance, the canonical CS set  $\{|R_i, P_i\rangle\}$  is quasi-classical with respect to a 1-D harmonic oscillator Hamiltonian  $\hat{H}_{HO}$  with mass  $m_i$  and angular frequency  $\omega_i$  [27,39]. In contrast, the Thouless CS set is not quasi-classical with respect to the electronic Hamiltonian  $\hat{H}_e$  or to any other chemically relevant Hamiltonian. The divergent quasi-classical status of the canonical and Thouless CS sets is somewhat reflected by the fact that they lead in SL-END to classical and quantum dynamics for the nuclei and electrons, respectively. A great advantage of quasi-classical CS sets is that they permit reconstructing some degree of quantum description from classical dynamics [15,16,28]. In SL-END, the zero-width limit applied to all the Gaussian wave packets (= canonical CS) of  $|\Psi_N\rangle$  renders them as Dirac delta functions that lose most of the quantum nature of the original finite-width wave packets. The CS quantum reconstruction procedure for SL-END can be illustrated for the case of the vibrational motion of a diatomic molecule AB simulated with SL-END [15,16]. At any time of that vibration, a canonical CS (= Gaussian wave packet)  $|Z_{Vib}\rangle$ ,  $Z_{Vib} = \sqrt{m_{AB} \omega_{AB} / 2} R_{Vib} + i \sqrt{1/2m_{AB} \omega_{AB}} P_{Vib}$ ,

with mass  $m_{AB}$  and angular frequency  $\omega_{AB}$  corresponding to the molecule AB effective mass and vibrational angular frequency, respectively, can be reconstructed so that its quasi-classical vibrational motion in terms of its parameters  $R_{Vib}$  and  $P_{Vib}$  matches completely the SL-END classical vibrational motion of AB along its bond (*i.e.*,  $R_{Vib}(t) = \Delta R_{AB}(t)$  and  $P_{Vib}(t) = P_{AB}(t)$  thenceforth). Moreover, that dynamically matched canonical CS admits a resolution into the vibrational eigenstates  $|v\rangle$ ,  $v=0, 1, 2, \dots$ ) of the molecule AB [27]

$$|Z_{Vib}\rangle = \exp\left(-\frac{1}{2}|Z_{Vib}|^2\right) \sum_{v=0}^{\infty} \frac{Z_{Vib}^v}{\sqrt{v!}} |v\rangle. \quad (11)$$

Therefore, the probability  $P_v$  to find the SL-END-simulated molecule AB in its vibrational eigenstate  $|v\rangle$  is given by a Poisson distribution

$$\begin{aligned} P_v &= \exp(-|Z_{Vib}|^2) \frac{|Z_{Vib}|^{2v}}{v!} \\ &= \exp(-E_{Vib}/\omega_{AB}) \frac{(E_{Vib}/\omega_{AB})^v}{v!}; \\ E_{Vib} &= \omega_{AB}|Z_{Vib}|^2 = \frac{1}{2m_{AB}} P_{AB}^2 + \frac{1}{2} m_{AB} \omega_{AB}^2 R_{AB}^2 \end{aligned} \quad (12)$$

where  $E_{Vib}$  is the SL-END classical vibrational energy of the molecule AB. Notice that in this quantum reconstruction procedure a molecule in the vibrational ground state  $|0\rangle$  corresponds to a zero SL-END vibrational motion ( $E_{Vib}=0 \Rightarrow P_v = \delta_{0v}$  in Equation (12)). The described quantum reconstruction procedure for the vibration of a diatomic molecule can be generalized straightforwardly to each of the vibrational normal modes of a polyatomic molecule [36]. The reconstructed quantum vibrational probabilities from SL-END are accurate for the case of vibrations induced on molecules by collisions with ions or atoms at intermediate and high collision energies (see Section 2.3 for examples). The described quantum reconstruction procedure assumes classical harmonic vibrations in the simulated molecules; those vibrations can be properly matched with the quasi-classical harmonic vibrations of the canonical CS based on a harmonic Hamiltonian  $\hat{H}_{HO}$ . In case of anharmonic vibrations, CS sets based on anharmonic Hamiltonians can be used instead [36] (e.g. Nieto CS set based on the Morse potential [40]).

The reconstruction of some degree of quantum description for classical nuclear vibrations [15,16] prompted the question about whether an analogous procedure can be devised for classical nuclear rotations. That question was answered positively with the development of a nearly quasi-classical

rotational CS set  $\{|xyz\rangle\}$  [28]:

$$\begin{aligned} |xyz\rangle &= \exp\left[-\frac{1}{2}|y|^2(1+|x|^2)^2(1+|z|^2)^2\right] \\ &\times \sum_{IMK} \left\{ \frac{[(2I!)]^2}{(I+M)!(I-M)!(I+K)!(I-K)!} \right\}^{1/2} \\ &\times \frac{x^{I(M)} y^{I(K)} |IMK\rangle}{(I!)^{1/2}} \end{aligned} \quad (13)$$

where  $x$ ,  $y$ , and  $z$  are the CS complex parameters, and  $|IMK\rangle$  ( $I=0, 1, 2, \dots$ ;  $M, K=0, \pm 1, \pm 2, \dots, \pm I$ ) are the eigenstates of a symmetric-rotor Hamiltonian  $\hat{H}_{Rot}$ .  $\{|xyz\rangle\}$  also admits an equivalent real parameterization [28]. This rotational CS set was developed from an earlier rotational CS set formulated by Janssen [33]. The Janssen rotational CS set involved abstract rotational eigenstates  $|IMK\rangle$  with both integer and half-integer quantum numbers ( $I=0, 1/2, 1, 3/2, \dots$  etc.) and was therefore inapplicable to rotations in real space. Conversely, the present rotational CS involves eigenstates  $|IMK\rangle$  with integer quantum number alone and is therefore applicable to rotations in real space. Both Janssen and the present rotational CS sets have indefinite measures whose expressions can be found in Refs. [33] and [28], respectively. The present rotational CS  $|xyz\rangle$  evolves quasi-classically with the symmetric-rotor Hamiltonian  $\hat{H}_{Rot}$  for a short period of time if the CS total angular momentum average estimated as  $\langle xyz | \hat{L}^2 | xyz \rangle^{1/2}$  satisfies the condition:  $\langle xyz | \hat{L}^2 | xyz \rangle^{1/2} \gg \hbar$  (Atomic units are dropped in that comparison) [28]. In that regime, the rotational CS obeys the Euler equations of rotation from classical mechanics [14,28]. The condition  $\langle xyz | \hat{L}^2 | xyz \rangle^{1/2} \gg \hbar$  is met by the relatively fast rotations induced on molecules by collisions with ions or atoms at intermediate and high collision energies. With the present rotational CS set, a CS quantum reconstruction procedure for classical rotations [28] can be conducted similarly to that for classical vibrations. Suppose that the rotation of a symmetric-rotor molecule is simulated via SL-END with a total classical angular momentum  $\gg \hbar$ ; then, at any moment of that simulation, a rotational CS  $|xyz\rangle$  can be reconstructed so that its quasi-classical rotation matches the classical SL-END rotation of the molecule. Then, the probability  $P_{IMK}$  to find the SL-END-simulated symmetric-rotor molecule in its rotational eigenstate  $|IMK\rangle$  is (cf. Equation (13)) [28]

$$\begin{aligned} P_{IMK} &= \exp\left[-|y|^2(1+|x|^2)^2(1+|z|^2)^2\right] \\ &\times \frac{[(2I!)]^2}{(I+M)!(I-M)!(I+K)!(I-K)!} \\ &\times \frac{|x|^{2(I+M)} |y|^{2I} |z|^{2(I+K)}}{I!} \end{aligned} \quad (14)$$

Notice that in this quantum reconstruction procedure a symmetric-rotor molecule in its rotational ground state  $|000\rangle$  corresponds to a zero SL-END rotational motion ( $E_{Rot} = 0 \Rightarrow x = y = z = 0 \Rightarrow P_{IMK} = \delta_{0I} \delta_{0M} \delta_{0K}$  in Equation (14) [28]). Cases with spherical-rotor and linear molecules are subcases that can be treated in a similar way [28]. More details about this rotational CS set will be given in Section 2.3.

The CS reconstruction of vibrational and rotational quantum probabilities is relevant for the calculation of vibrationally- and rotationally-resolved properties from SL-END simulations [15,16,28]. However, that CS procedure cannot reconstruct extreme quantum phenomena such as tunnelling. For those cases, more involved approaches are necessary (e.g. to adopt a higher-level END model with at least a nuclear single-determinantal wavefunction [3]).

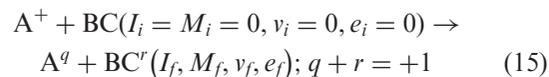
The Thouless CS set does not exhibit a quasi-classical behaviour with the electronic Hamiltonian. However, that is expected since that CS set should describe quantum electronic dynamics. Nonetheless, a new CS procedure connecting quantum and classical descriptions for electrons has been recently developed [35]; that new CS aspect is discussed in Section 3.

### 2.3. Utilization of CS sets in the SL-END theory

After having reviewed the CS sets relevant to SL-END, their specific utilization in that theory can be discussed. As stated in the Introduction, one of the roles of the canonical and the Thouless CS sets is to represent the total trial SL-END wavefunction  $|\Psi_{SL-END}\rangle$  so that their CS parameters as the  $|\Psi_{SL-END}\rangle$  variational parameters define an adequate phase space for the SL-END dynamical equations via the TDVP. From its inception, SL-END has the canonical and the Thouless CS included in its formalism to attain those dynamical features; that CS aspect of SL-END has been discussed in detail in Section 2.1.

As discussed in the Introduction, the SL-END method is very accurate to simulate ion-molecule and atom-molecule collisions at intermediate and high collision energies. However, numerous experiments on those systems report quantum rotationally- and/or vibrationally-resolved properties that the nuclear classical dynamics of SL-END cannot reproduce. That shortcoming in the original SL-END method was overcome through the development of the CS quantum reconstruction procedures [15,16,28] explained in Section 2.2. It is quite instructive to outline now how those CS procedures are applied to the calculation of rotationally- and vibrationally-resolved

cross sections of ion-molecule and atom-molecule collisions. Let us consider a travelling atomic ion  $A^+$  (projectile) colliding with a diatomic molecule BC (target) for the sake of illustration:



where BC is initially at rest in its rotational, vibrational, and electronic ground states; those initial conditions are usual in many ion-molecule reactions. Although the example does portray rearrangement processes (e.g.  $A^+ + BC(I_i = M_i = 0, v_i = 0, e_i = 0) \rightarrow B^q + AC^r(I_f, M_f, v_f, e_f); q + r = +1$ , etc.), those cases can be treated similarly to the present non-rearrangement case. At the initial and final times of a SL-END simulation, the projectile and target are so separated that can be considered as isolated species. For the initial and final isolated target BC in a SL-END simulation, its nuclear part  $|\Psi_N^{BC}\rangle$  of its SL-END wavefunction  $|\Psi_{SL-END}^{BC}\rangle = |\Psi_N^{BC}\rangle |\Psi_e^{BC}\rangle$  can be reconstructed with finite widths  $\Delta R_i$  by matching the positions and momenta  $\{R_i, P_i\}$  of  $|\Psi_N^{BC}\rangle$  with those from the SL-END simulation in the zero-widths limit (cf. Equation (4)). Then, the reconstructed  $|\Psi_N^{BC}\rangle$  can be approximately factorized into translational  $|\Psi_{Trans}^{BC}\rangle$ , rotational  $|\Psi_{Rot}^{BC}\rangle$ , and vibrational  $|\Psi_{Vib}^{BC}\rangle$  parts so that the SL-END wavefunction  $|\Psi_{SL-END}^{BC}\rangle$  becomes [28,36]

$$|\Psi_{SL-END}^{BC}\rangle = |\Psi_N^{BC}\rangle |\Psi_e^{BC}\rangle = |\Psi_{Trans}^{BC}\rangle |\Psi_{Int}^{BC}\rangle |\Psi_e^{BC}\rangle \approx |\Psi_{Trans}^{BC}\rangle |\Psi_{Rot}^{BC}\rangle |\Psi_{Vib}^{BC}\rangle |\Psi_e^{BC}\rangle \quad (16)$$

where  $|\Psi_{Int}^{BC}\rangle \approx |\Psi_{Rot}^{BC}\rangle |\Psi_{Vib}^{BC}\rangle$  contains the parts corresponding to the internal nuclear degrees of freedom. The lengthy details of the above factorization are given in [28,36]. In brief, that factorization starts with a change from the original SL-END nuclear canonical variables  $\{R_i, P_i\}$  in the laboratory frame to those of the centre of mass and of the internal motions of BC [28,36]. With that change of canonical variables, it is possible to factorize  $|\Psi_N^{BC}\rangle$  as  $|\Psi_N^{BC}\rangle = |\Psi_{Trans}^{BC}\rangle |\Psi_{Int}^{BC}\rangle$ , where  $|\Psi_{Trans}^{BC}\rangle$  is a 3-D wave packet describing the centre of mass translational motion, and  $|\Psi_{Int}^{BC}\rangle$  is an intricate 3-D wave packet describing the internal nuclear motions. Then, it is possible to replicate in  $|\Psi_{Int}^{BC}\rangle$  the approximate separation of the rotational and vibrational degrees of freedom that is customarily used in elementary spectroscopy [41]. In that approach, the rovibrational wavefunction of a molecule BC can be approximated as the product of independent vibrational  $|\nu\rangle$  and rotational  $|IM\rangle = |IM0\rangle$  wavefunctions (Rovibrational coupling and centrifugal distortion effects are therefore neglected.). In that way,  $|\Psi_{Int}^{BC}\rangle$  can be approximately factorized as  $|\Psi_{Int}^{BC}\rangle \approx |\Psi_{Rot}^{BC}\rangle |\Psi_{Vib}^{BC}\rangle$ ,

where  $|\Psi_{Vib}^{BC}\rangle$  is 1-D wave packet (= canonical CS) describing the vibrational motion of BC, and  $|\Psi_{Rot}^{BC}\rangle$  is an intricate function describing the rotational motion of BC [28,36].  $\Psi_{Rot}^{BC}$  that can be approximated by the rotational CS of Section 2.2 [28,36], an approach adopted here henceforth. At the final time of a SL-END simulation, the final and factorized SL-END wavefunction  $|\Psi_{SL-END}^{BC(f)}\rangle$  of the isolated molecule BC can be projected onto a wavefunction  $|\Phi^{(f)}\rangle = |\Phi_{Trans}^{(f)}\rangle |\Phi_{Rot}^{(f)}\rangle |\Phi_{Vib}^{(f)}\rangle |\Phi_e^{(f)}\rangle$ , where  $|\Phi_{Trans}^{(f)}\rangle$  is a frozen, narrow-width, 3-D wave packet travelling in the same scattering direction as the final BC molecule.  $|\Phi_{Trans}^{(f)}\rangle$  carries selected nuclear rotational  $|\Phi_{Rot}^{(f)}\rangle = |I_f M_f\rangle = |I_f M_f 0\rangle$  and vibrational  $|\Phi_{Vib}^{(f)}\rangle = |v_f\rangle$  eigenstates and a selected electronic HF single-determinantal state  $|\Phi_e^{(f)}\rangle = |e_f\rangle$  of the molecule BC in its final configuration. That projection renders the probability amplitude  $A_{BC}^{(f)}$  to find the final molecule in the mentioned eigenstates and state [36]:

$$A_{BC}^{(f)} = \left\langle \Phi_{Trans}^{(f)} \Phi_{Rot}^{(f)} \Phi_{Vib}^{(f)} \Phi_e^{(f)} \left| N^{-1/2} \Psi_{SL-END}^{BC(f)} \right. \right\rangle \\ = A_{Trans}^{(f)} A_{Rot}^{(f)} A_{Vib}^{(f)} A_e^{(f)} \exp(iA_{SL-END}) \quad (17)$$

where  $N^{-1/2}$  is the normalization constant of  $|\Psi_{SL-END}^{BC(f)}\rangle$ ,  $A_{Degree}^{(f)} = \langle \Phi_{Degree}^{(f)} | \Psi_{SL-END}^{BC(f)} \rangle$  (Degree = translational, rotational, vibrational, and electronic) is the probability amplitude of each degree of freedom, and  $A_{SL-END}$  is the SL-END action [28,36] (cf. Equation (1)).  $|A_{Trans}^{(f)}|^2$  is basically a Dirac delta function centred at the final centre of mass position of BC [36] that renders a value of one in the cases considered below.  $|A_{Rot}^{(f)}|^2 = P_{I_f M_f} = P_{I_f M_f 0}$  and  $|A_{Vib}^{(f)}|^2 = P_{v_f}$  are the rotational and vibrational CS probabilities to find the final molecule BC in its rotational and vibrational eigenstates  $|I_f M_f\rangle = |I_f M_f 0\rangle$  and  $|v_f\rangle$ , respectively (cf. Equations (12) and (14), respectively), and  $|A_e^{(f)}|^2 = P_{e_f}$  is the probability to find the final molecule BC in the HF single-determinantal state  $|\Phi_e^{(f)}\rangle = |e_f\rangle$ . If BC transfers electrons from or to  $A^+$  (e.g.  $A^+ + BC$  ( $I_i = M_i = 0, v_i = 0, e_i = 0$ )  $\rightarrow$   $A + BC^+(I_f, M_f, v_f, e_f)$  or  $\rightarrow A^{2+} + BC^-(I_f, M_f, v_f, e_f)$ , etc.),  $|A_e^{(f)}|^2 = P_{e_f}$  is related to the probability that those electron-transfer processes occur. The same factorization and projection procedures can be applied to the initial isolated molecule BC. Considering the process in Equation (15), the initial molecule BC is prepared in its rotational  $|I_i = 0 M_i = 0\rangle = |I_i = 0 M_i = 0 K = 0\rangle$ , vibrational  $|v_i = 0\rangle$ , and electronic  $|e_i = 0\rangle$  ground states so that the probability to find the molecule in that state is  $P_{I_i=0, M_i=0, v_i=0, e_i=0} = |A_{BC}^{(i)}|^2 = 1$  (cf. Equation (17)). At the final time, the probability to find the molecule in the rotational  $|I_f M_f\rangle = |I_f M_f K = 0\rangle$ , vibrational  $|v_f\rangle$ , and electronic  $|e_f\rangle$  eigenstates/state is

$P_{I_f, M_f, v_f, e_f} = |A_{BC}^{(f)}|^2 = |A_{Rot}^{(f)}|^2 |A_{Vib}^{(f)}|^2 |A_e^{(f)}|^2 = P_{I_f M_f}^{(f)} P_{v_f}^{(f)} P_{e_f}^{(f)}$ . Therefore, the probability amplitude and probability of the transition:  $I_i = 0 \rightarrow I_f$ ,  $M_i = 0 \rightarrow M_f$ ,  $v_i = 0 \rightarrow v_f$ , and  $e_i = 0 \rightarrow e_f$  are  $A_{BC}^{(f)}$  and  $P_{I_f, M_f, v_f, e_f} = |A_{BC}^{(f)}|^2$ , respectively. The probability amplitude  $A_{BC}^{(f)}$  thus interpreted enters into the calculation of state-resolved cross-sections (cf. Equation (18))

The SL-END calculation of state-resolved cross sections requires cross section expressions compatible with the SL-END classical nuclear dynamics. Those expressions are the semiclassical cross sections that are obtained from their corresponding quantum expressions evaluated in the limit of  $\hbar \rightarrow 0$  (Atomic units are dropped in that expression) with different semiclassical techniques [42,43]. In many scattering situations with SL-END, differential cross sections (DCS)  $d\sigma^{i \rightarrow f}(\theta)/d\Omega$  can be accurately evaluated with the following semiclassical expression obtained from its corresponding quantum DCS expression through the stationary phase approximation [42,43]

$$\frac{d\sigma^{i \rightarrow f}(\theta)}{d\Omega} = \left| \sum_{m=1}^N f_m(\theta) \right|^2 = \left| \sum_{m=1}^N b_m^{1/2} A_{BC}^{(f)}(b_m) \right. \\ \left. \times \left\{ \sin[\theta(b_m)] \left[ \frac{d\theta(b)}{db} \right]_{b=b_m} \right\}^{-1/2} \right|^2 \quad (18)$$

where  $\theta(b)$  is the scattering angle of the final projectile  $A^q$  as a function of its initial impact parameter  $b$ ;  $b_m$  are the impact parameters of the  $m$  ( $1 \leq m \leq N$ ) classical trajectories ('branches') that end up with  $A^q$  scattered into the angle  $\theta(b_m)$  and with a scattering amplitude  $f_m(\theta)$ . However, the previous expression exhibits unphysical singularities at angles  $\theta_R = \theta(b_R)$  where  $[d\theta(b)/db]_{b=b_R} = 0$  (rainbow angle singularity [42,43]) and where  $\theta = 0^\circ$  or  $180^\circ$  (forward and backward glory angle singularities, respectively [42]). On and near those scattering directions, other semiclassical DCS expressions obtained with techniques more sophisticated than the stationary phase approximation used for Equation (18) are required (e.g., the transitional Airy, uniform Airy, transitional Pearcey, and uniform Pearcey approximations for rainbow angle singularities [43]; glory angle corrections [42], etc.). The utilization of those semiclassical techniques to evaluate DCS from SL-END simulations are discussed in detail in [36]. The most common DCS singularity is that of a single rainbow angle  $\theta_R$  produced by the coalescence of two close scattering trajectories in the direction  $\theta_R$ . For that case, the most accurate semiclassical approximation is the uniform Airy approximation [42,43]. In that approach, the two scattering amplitudes  $f_m(\theta)$  in Equation (18)

corresponding to the coalescing trajectories (say, those with  $m=2$  and 3) are replaced by one scattering amplitude  $f_{23}^{\text{U,Airy}}(\theta)$  [43]

$$f_{23}^{\text{U,Airy}}(\theta) = \pi^{1/2} \exp\left[i\left(A_{23} - \frac{1}{4}\pi\right)\right] \left[ B_+(\theta) \xi_{23}^{1/4} Ai(-\xi_{23}) - iB_-(\theta) \xi_{23}^{-1/4} Ai'(-\xi_{23}) \right];$$

$$B_{\pm}(\theta) = |f_2(\theta) \pm |f_3(\theta)| \quad (19)$$

where  $A_{23}(\theta)$  and  $\xi_{12}(\theta)$  are functions of the SL-END action along the two close trajectories, and  $Ai$  and  $Ai'$  the Airy function and its first derivative [43]. A uniform-airy DCS does not exhibit an unphysical rainbow angle singularity at  $\theta_R$ , but instead it exhibits a bounded rainbow angle peak at a slightly different scattering direction  $\theta$  in agreement with experiments. More complicated situations involving a higher number and/or different types of singularities can be treated satisfactorily with more sophisticated semiclassical techniques [42,43]. A pedagogical account of the semiclassical evaluation of DCS from SL-END simulations is given in Ref. [21]. Semiclassical integral cross sections (ICS) can be evaluated in a similar way [36,42].

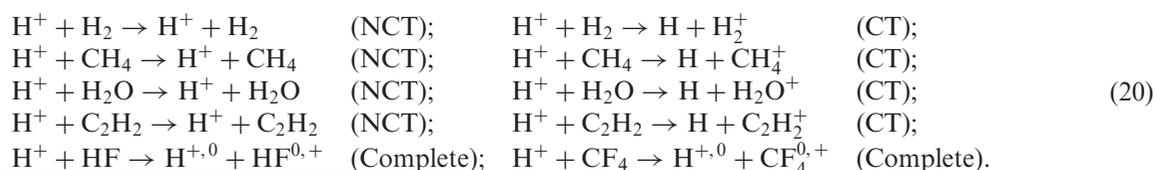
The described CS procedure to evaluate state-resolved cross sections with SL-END has been successfully applied to a great variety of ion-molecule collisions at intermediate collisional energies. A first application was an exhaustive SL-END study of the benchmark system  $\text{H}^+ + \text{H}_2$  at  $E_{\text{Lab}}=30$  eV [15,16]. The main quantitative results from that study were vibrationally-resolved DCS and ICS ( $A_{\text{BC}}^{(f)} = A_{\text{vib}}^{(f)}$ ) for the non-charge-transfer processes  $\text{H}^+ + \text{H}_2$  ( $v_i = 0$ )  $\rightarrow$   $\text{H}^+ + \text{H}_2$  ( $v_f = 0, 1, 2, 3, 4$ ). Those calculated results were in excellent agreement with available experimental data [15,16] and performed better than other theoretical results with the transition surface hopping model and the infinite order sudden approximation [15,16]. That study firmly demonstrated the accuracy of the canonical CS quantum reconstruction procedure within SL-END to calculate the mentioned properties. The same approach was employed to calculate total (i.e. non-vibrationally- and non-rotationally-resolved) non-charge-transfer (NCT), charge-transfer (CT), and complete (=NCT+CT) DCS in the following systems at  $E_{\text{Lab}}=30$  eV [15–18,20–22,36]:

All those calculated DCS compared well with available experimental results [15–18,20–22,36]. In the first three systems listed in Equation (20), calculations of energy transfers for the NCT processes were also performed [15–18]. Those calculations are closely related to those of the NCT DCS. The calculated energy transfers compared satisfactorily with available experimental results [15–18]. Finally, calculations of rotationally-resolved DCS ( $A_{\text{BC}}^{(f)} = A_{\text{rot}}^{(f)}$ ) in ion-molecule and atom-molecule collisions are currently underway in the author's research group.

### 3. Present CS efforts with the SL-END theory

The previous CS aspects and capabilities of SL-END can stimulate further explorations and developments. In fact, those capabilities have utilized only a fraction of the various resources available in the vast realm of the CS theory [27]. Many additional CS efforts within the END framework can be conceived. However, only a few CS-END efforts under development in the author's research group will be discussed here. Those efforts include: (1) A time-dependent (TD) Kohn–Sham (KS) density-functional-theory (DFT) direct-dynamic method in the END framework, named END/KSDFT henceforth [37,44], (2) a novel CS approach to classical-electrostatics charge-equilibration models [35], and (3) a CS path-integral approach [27] to END.

An obvious disadvantage of SL-END is its exclusion of important electron correlation effects. One way to overcome that limitation is to go beyond the SL-END single-determinantal representation and incorporate post-Hartree–Fock methods [10] into the END framework (e.g. a multi-configurational representation [11]) as exemplified by the higher-level END models [3]. However, the resulting dynamical equations from those models will be computationally expensive. Alternatively, a more feasible approach is to retain the SL-END single-determinantal representation and include electron correlation via the TDKSOFT [45–48]. That approach leads to the new END/KSDFT method [37,44]. Like SL-END [1–3], END/KSDFT adopts a classical-mechanics description for the nuclei and a quantum single-determinant representation for the electrons. More precisely, the



END/KSDFT wavefunction is formally identical to the SL-END one:  $|\Psi_{\text{END/KSDFT}}\rangle = |\Psi_N\rangle|\Psi_e\rangle$  [37], but now the Thouless single-determinant state  $|\Psi_e\rangle = |\mathbf{z}, \mathbf{R}\rangle$  is interpreted as a KS wavefunction [37,45–48]. Thus,  $|\mathbf{z}, \mathbf{R}\rangle$  through reference to an auxiliary system of non-interacting electrons provides its density  $\rho(\mathbf{r}; \mathbf{z}, \mathbf{z}^*, \mathbf{R})$  as the exact electron density of the actual system of interacting electrons if the exchange-correlation potential  $v_{xc}[\rho](\mathbf{r}, t)$  (or, equivalently, the exchange-correlation part of the action  $A_{xc}[\rho]$ ) is known exactly [37,45–48]. In practice, neither  $v_{xc}[\rho](\mathbf{r}, t)$  nor  $A_{xc}[\rho]$  is known in an exact form, but various good approximations to them are available [46–48]. Following TDKSDFT prescriptions, the SL-END Lagrangian, Equation (6), can be transformed into the END/KSDFT Lagrangian  $L_{\text{END/KSDFT}}[\mathbf{R}, \mathbf{P}, \rho] = L_{\text{END/KSDFT}}[\mathbf{R}, \mathbf{P}, \mathbf{z}, \mathbf{z}^*]$  if its electronic part  $E_e[\mathbf{R}, \mathbf{z}, \mathbf{z}^*]$  is recast into a TDKSDFT form [45–48]:

$$\begin{aligned}
 E_e^{\text{END/KSDFT}}[\mathbf{R}, \mathbf{z}, \mathbf{z}^*] &= \frac{\langle \mathbf{z}, \mathbf{R} | \hat{T}_e | \mathbf{z}, \mathbf{R} \rangle}{\langle \mathbf{z}, \mathbf{R} | \mathbf{z}, \mathbf{R} \rangle} + \int d\mathbf{r} \rho(\mathbf{r}; \mathbf{z}, \mathbf{z}^*, \mathbf{R}) v_{\text{ext}}(\mathbf{r}; \mathbf{R}) \\
 &+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}; \mathbf{z}, \mathbf{z}^*, \mathbf{R}) \rho(\mathbf{r}'; \mathbf{z}, \mathbf{z}^*, \mathbf{R})}{|\mathbf{r} - \mathbf{r}'|} \\
 &+ E_{xc}^{gs}[\rho(\mathbf{r}; \mathbf{z}, \mathbf{z}^*, \mathbf{R})] \quad (21)
 \end{aligned}$$

whose terms are the KS kinetic, external-potential, classical self-repulsion, and exchange-correlation energies, respectively. The external potential  $v_{\text{ext}}(\mathbf{r}; \mathbf{R}) = -\sum_{i=1}^{N_N} Z_i |\mathbf{r} - \mathbf{R}_i|^{-1}$  is caused by the moving classical nuclei. In Equation (21) the adiabatic approximation to  $A_{xc}[\rho]$  [46–48] is employed since  $E_{xc}^{gs}[\rho]$  is any of the available ground-state, time-independent, KSDFT exchange-correlation energy functionals. In the adiabatic approximation, the exchange-correlation part of the action is  $A_{xc}[\rho] \approx A_{xc}^{\text{adia.}}[\rho] = \int_{t_1}^{t_2} dt E_{xc}^{gs}[\rho]$ , and the exchange-correlation potential  $v_{xc}[\rho](\mathbf{r}, t) \approx v_{xc}^{\text{adia.}}[\rho](\mathbf{r}, t) = v_{xc}^{gs}[\tilde{\rho}](\mathbf{r})|_{\tilde{\rho}(\mathbf{r})=\rho(\mathbf{r}, t)}$ , where  $v_{xc}^{gs}[\rho](\mathbf{r})$  is any of the available ground-state, time-independent exchange-correlation potentials. The adiabatic approximation is extensively used in linear-response TDKSDFT calculations of excitation energies [46–48]. In dynamics, the adiabatic approximation was employed in the TDKSDFT direct-dynamics method by Theilhaber [49], where it rendered satisfactory dynamical results. By construction, the adiabatic approximation should work well with slow-evolving electron densities that remain near the ground state. However, previous TDKSDFT experience [47,48] suggests that the adiabatic approximation, even in its harsher local-density form [46–48], can work acceptably with some processes beyond the slow and near-ground-state regime. In addition, the adiabatic approximation leads to causal exchange-correlation

kernels [46–48]. For those reasons, the adiabatic approximation is suitably adopted for the first version of END/KSDFT. More accurate approximations to  $A_{xc}[\rho]$  [46–48] will be tried in the future. The application of the TDVP to the END/KSDFT action  $A_{\text{END/KSDFT}}[\mathbf{R}, \mathbf{P}, \rho] = A_{\text{END/KSDFT}}[\mathbf{R}, \mathbf{P}, \mathbf{z}, \mathbf{z}^*]$  associated with the END/KSDFT Lagrangian leads to the END/KSDFT dynamical equations [37]. Those equations outwardly look like the SL-END ones, Equations (8) and (9), but have all its terms recast in a TDKSDFT form.

The END/KSDFT method will be very useful for the dynamical simulation of large chemical systems with inclusion of electron correlation effects at a relatively low computational cost. Through END/KSDFT, the Thouless CS set encounters the new application of representing a single-determinantal state in a TDKSDFT dynamical context. A preliminary result of the END/KSDFT method is given in Figure 1. There, four snapshots of an END/KSDFT/B3LYP/6-31G\*\* simulation of the  $\text{H}^+ + \text{HF}$  collision at  $E_{\text{Lab}} = 30$  eV is shown. In Figure 1, the small balls represent the nuclei (green ball = F, gray balls = H) and the coloured clouds, electron density isosurfaces increasing in value through the sequence: blue, green, yellow, and red. The snapshots correspond to four different times of a simulated process lasting 24.2 fs (1000 a.u. of time). The  $\text{H}^+$  projectile coming from the left collides with the upright HF molecule ( $\text{H}_F$ ) causing rotational, vibrational, and electronic excitations on the target during its flyby. Although temporary electron transfers from HF to  $\text{H}^+$  occur during the reactants' closest approach, the scattered projectile leaves the HF molecule as  $\text{H}^+$  without gaining an electron. Additional theoretical details of the END/KSDFT method along with its applications to relevant chemical systems are given in Ref. [37].

The canonical and rotational CS sets have been used to reconstruct some level of quantum description from the classical nuclear dynamics of SL-END simulations [15,16,28]. In those procedures, the involved CS sets establish connections between quantum- and classical-mechanics descriptions of the nuclear degrees of freedom. The Thouless CS set did not play such a quantum-classical mediating role in SL-END because its role was to describe a quantum electronic dynamics. However, in the context of the so-called quantum/classical (Q/C) methods [50–57], classical electronic descriptions are routinely adopted for the peripheral region of large systems as a way to reduce the computational cost. In some Q/C methods, that classical electronic description entails classical-electrostatics charge densities in lieu of

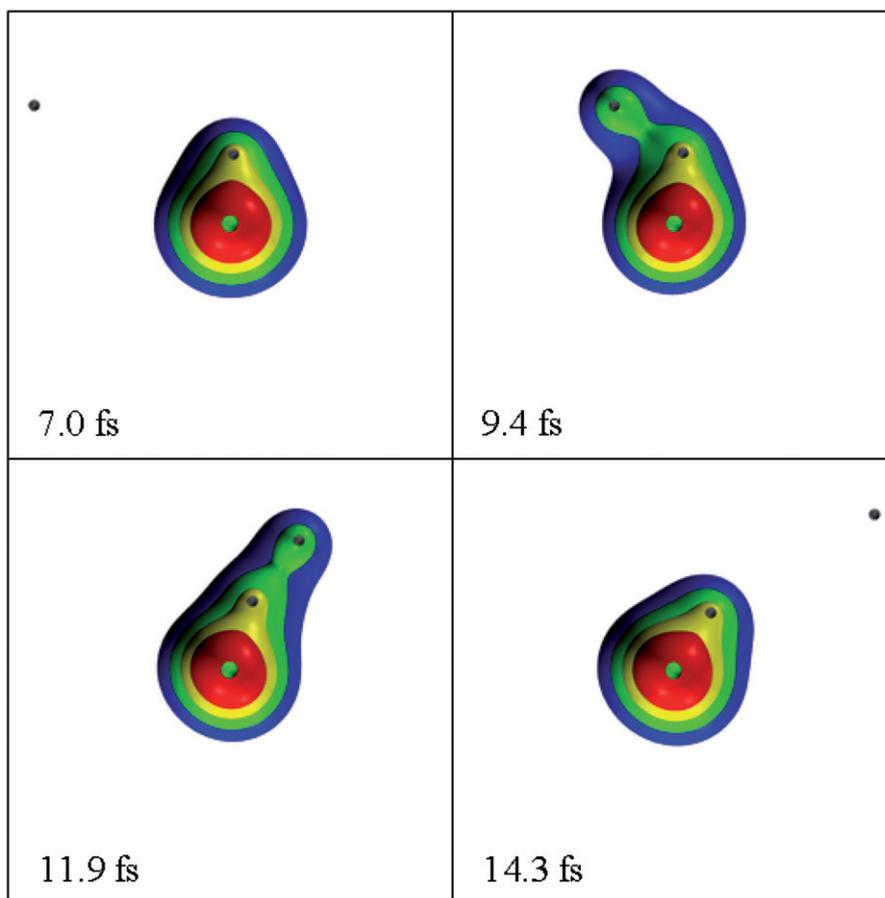


Figure 1. Four snapshots of an END/KSDFT/B3LYP/6-31G\*\* simulation of  $H^+ + HF$  at  $E_{Lab} = 30$  eV. Snapshot times are shown in fs. The small balls represent the nuclei (green ball = F, black balls = H) and the coloured contours, electron density isosurfaces increasing in value through the sequence: blue, green, yellow, and red. The snapshots show an inelastic scattering process. [This figure can be viewed in colour online.]

quantum wavefunctions and/or quantum electron densities. For instance, the charge equilibration (CE) [56,57] model represents the atoms in a molecule as a set of fluctuating charges in a classical-electrostatics fashion. In a system of  $N_{Atom}$  atoms having atomic charges:  $\{Q_A, Q_B, \dots, Q_{N_{Atom}}\}$ , the CE energy  $E_{Molecule}^{CE}$  is [57]

$$\begin{aligned}
 E_{Molecule}^{CE}(Q_A, Q_B, \dots, Q_{N_{Atom}}) &= \sum_A^{N_{Atom}} (E_{A^0} + \chi_A^* Q_A + \eta_A^0 Q_A^2) \\
 &+ \sum_{A < B}^{N_{Atom}} J_{AB}^{CE}(R_{AB}) Q_A Q_B \quad (22)
 \end{aligned}$$

where  $E_{A^0}$  are the neutral atom energies,  $\chi_A^*$  environment-perturbed Mulliken electronegativities,  $\eta_A^0$  absolute atomic hardnesses, and  $J_{AB}^{CE}(R_{AB}) = J_{AB}(R_{AB}) = (\phi_A \phi_A | \phi_B \phi_B)$  Coulomb integrals of the atomic orbitals on atoms A and B at separation  $R_{AB}$ .

While the previous terms still have a quantum-mechanical origin, the energy expression  $E_{Molecule}^{CE}$  is in a classical-electrostatics form. This prompts the question about whether it is possible to formulate a CS procedure analogous to those for the nuclear case that can establish a connection between quantum and classical-electrostatics descriptions for the electronic degrees of freedom. Notice that in this new context one is not interested in reconstructing a quantum description from a classical one, but conversely in extracting a convenient classical description from a quantum one. The answer to that question for the case of the CE model is positive: such a procedure exists [35] and involves a CS set formulated with valence-bond (VB) [10] states. In that CS/VB approach [35], a generalized CE model is obtained from a quantum VB model in conjunction with the CS theory by a series of well-defined rules and approximations. That generalized CE model contains the traditional CE model as a subcase. However, unlike its CE subcase, the generalized CE

model can provide a satisfactory charge-transfer description at molecular dissociations that allows the use of that model for reactive processes. Moreover, the formulation of the generalized CE model demonstrated for the first time that the CE charges and CE Coulomb interaction terms ( $J_{AB}^{CE}(R_{AB})Q_AQ_B$  in Equation (22)) have their origin in the VB Mulliken charges and VB atomic interaction terms, respectively. Those precise demonstrations overcame previous CE phenomenological derivations of the CE charges and CE Coulomb interaction terms. The CS/VB approach will play a key role in incorporating the CE model and other electronic hybrid Q/C methods into the END framework. The resulting END/Q/C methodologies will be computationally efficient to simulate the dynamics of large systems.

As mentioned in the Introduction, another possible role of the CS sets in SL-END is to derive the SL-END dynamical equations via the CS path-integral representation of the propagator [27]. The CS theory has a long and productive relationship with the path-integral approach to quantum mechanics [27], but there have been no attempts to connect END with that approach thus far. Following previous CS development [27], it would be possible to derive the SL-END dynamical equations via a CS path-integral approach that employs the CS sets associated with SL-END, especially the canonical and the Thouless CS sets. That approach to SL-END not only has a high theoretical value but also a practical one since it will bring about fruitful interactions between SL-END and established semiclassical methods that utilize the canonical CS set [29,30]. The CS path-integral approach to SL-END is currently under development in the author's research group.

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