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Electron-Nuclear Dynamics of Molecular Systems.

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ABSTRACT

The content of an *ab-initio* time-dependent theory of quantum molecular dynamics of electrons and atomic nuclei is presented. Employing the time-dependent variational principle and a family of approximate state vectors yields a set of dynamical equations approximating the time-dependent Schrödinger equation. These equations govern the time evolution of the relevant state vector parameters as molecular orbital coefficients, nuclear positions and momenta. This approach does not impose the Born-Oppenheimer approximation, does not use potential energy surfaces and takes into account electron-nuclear coupling. Basic conservation laws are fully obeyed. The simplest model of the theory employs a single determinantal state for the electrons and classical nuclei and is implemented in the computer code ENDyne. Results from this *ab-initio* theory are reported for ion-atom and ion-molecule collisions.

Introduction

Time-dependent theoretical methods are emerging important tools for the study of molecular processes. Explicit consideration of the time parameter makes it possible to follow, say, the detailed evolution of a reactive event from reactants to products and leads naturally to the theoretical determination of transition probabilities and rates. A limiting fact for most dynamics methods, both time-dependent and time independent ones is that they are based on electronic potential energy surfaces. The generation of a quality surface, let alone several, from first principles is a daunting task and only possible for small molecular systems. One often resorts to the construction of empirical and semi-empirical surfaces as the diatomics in molecule (DIM) surfaces. Although inexpensive to generate, such surfaces are not accurate for the study of detailed dynamics. If only a single such surface is used, as is often the case, then the dynamics of the electrons is neglected. Only by incorporating two or more surfaces and their couplings is the effect of electronic dynamics included [1].

There are approaches, such as the Close-Coupling method [2, 3] used in study of atomic and molecular collisions, where electronic dynamics is considered. However, these methods employ non-dynamical straight line or Coulomb nuclear trajectories and ignore the details of the nuclear dynamics. While fixed trajectories work well for collisional phenomena at energies above 1keV/amu, they lead to spurious dynamics at lower collision energies.

Another body of work has its origin in the approach to simulating annealing by Car and Parrinello [4]. This approach has been generalized to study dynamics of molecular systems or clusters [5, 6, 7] and uses a fictitious mass associated to the molecular orbital coefficients to generate newtonian-like equations for them in time. The method attempts to follow the lowest potential energy surface of the system, without having to perform an electronic optimization at each new nuclear geometry. Thus it is very much like dynamics on a single potential energy surface, but without the cost of generating the full surface.

The END (Electron Nuclear Dynamics) theory of Öhrn, Deumens, *et al* [8, 9, 10, 11] uses the time-dependent variational principle (TDVP) to generate equations that approximate the time-dependent Schrödinger equation and govern the time evolution of electronic and nuclear dynamical variables on a generalized phase space. The choice of trial wavefunction for the electrons and the nuclei determines the level of approximation. Both electrons and nuclei are treated fully dynamically including coupling terms. The dynamics of participating nuclei and electrons is subject to the instantaneous forces due to the full Coulomb interactions and there is no need to generate potential energy surfaces and associated stationary states.

A related method by Runge and Micha [12, 13] uses the Frenkel variational principle to derive equations for the electronic degrees of freedom and then use the eikonal approximation for the nuclei moving in the potential given by the electrons and the nuclear Coulomb repulsion. This method has been applied to proton-hydrogen and hydrogen-hydrogen collisions.

The simplest level of the END theory employs a single determinant for the electrons and the classical limit for the nuclei. This level of approximation has been implemented in a computer code ENDyne [14]. In spite of its simplicity this level of theory yields accurate results for transition probabilities, differential and total cross sections for a great variety of ion-atom and ion-molecule reactive collisions. The END theory for a multiconfigurational and for an antisymmetrized geminal power (AGP) electronic wavefunction has also been published [15, 16].

The next section gives an overview of the END theory and the conservation theorems. Section III discusses the effect of the nonadiabatic coupling terms. If these couplings are neglected, the calculation tends to follow a potential energy surface, in a Car-Parinello-like fashion. An example shows that dynamics without these terms are in disagreement with experiment. When the couplings are included agreement is excellent.

END Theory

The details of the END theory [9] and the associated ENDyne code [11] for the simplest level of theory are published, so it suffices here to give a summary survey to show the fundamental generality and pleasing structure of the dynamical equations.

The TDVP [17] for a full quantum approach requires stationarity of the action with the Lagrangian

$$L = \frac{\langle \Psi | \frac{i}{2}(\frac{d}{dt} - \frac{\overleftarrow{d}}{dt}) - H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{1}$$

where H is the full molecular Hamiltonian and Ψ the electronic-nuclear many-body wavefunction. The derivative $\frac{d}{dt}$ acts on the bra. The choice of trial wavefunction determines the details of the dynamical equations. Representing the nuclei by Gaussian wavepackets in the limit of zero widths results in a classical description with nuclear positions R and momenta P equivalent to employing the Lagrangian

$$L = \frac{1}{2} \sum_k \left(\vec{P}_k \cdot \dot{\vec{R}}_k - \dot{\vec{P}}_k \cdot \vec{R}_k \right) + \frac{\langle \Psi_{el} | \frac{i}{2}(\frac{d}{dt} - \frac{\overleftarrow{d}}{dt}) - H_{el} | \Psi_{el} \rangle}{\langle \Psi_{el} | \Psi_{el} \rangle}, \tag{2}$$

where the electronic Hamiltonian H_{el} includes the nuclear-nuclear repulsion. The END theory even admits a mixed approach with some of the nuclei treated by classical and others by quantum mechanics.

The full quantum TDVP approach with a completely general form of trial function yields the time-dependent Schrödinger equation. Restricting the trial wavefunction to a particular form leads to a set of coupled first-order differential equations [17, 9] governing the time evolution of the, in general, complex wavefunction parameters. The parameters assume the role of dynamical variables and form a generalized phase space. This phase space is not flat but has a nonunit metric and results in a Hamiltonian form of dynamical equations. The choice of wavefunction parameters becomes critical to ensure nonredundancy and continuous trajectories.

For the case of a single determinantal N-electron state vector Thouless [18] has provided the suitable parametrization. A Thouless determinant $|z\rangle$ is an antisymmetric product of nonorthogonal spin orbitals

$$\chi_h = \phi_h + \sum_{p=N+1}^{K} z_{ph} \phi_p, \tag{3}$$

which in END are expressed in terms of an atomic orbital basis set, $\{\phi_i;\ i=1,K\}$, centered on the nuclei. The molecular orbital coefficients $\{z_{ph}\}$ and their complex conjugates are the electronic dynamical variables. This form of wavefunction has the capacity to become any determinantal

of determinants at geometries R and R'.

The END theory yields a dynamics that satisfies the conservation laws of important physical quantities, as total energy, total momentum, and total angular momentum [9, 11]. The important conservation of total linear and angular momentum only holds when the electron-nuclear coupling terms are included.

Electron-Nuclear Coupling

The dynamical metric of Eq. (5) couples the electronic and nuclear degrees of freedom. The third row of the metric matrix has coupling terms that ensure the conservation of total momentum [9]. The theory must satisfy such conservation laws to be able to produce accurate detailed information about nuclear and electronic quantities. One might think that at higher energies the momentum of the nuclei overwhelms the contribution from the electrons when properties are computed, but that this is not the case is shown by our results.

The first row of the metric matrix couples the electronic degrees of freedom to the nuclear velocities. These coupling terms make up the matrix representation of the translation operator and provide the transformation of the z-coefficients as the centers of the basis functions move from one instant to the next. One could, alternatively, use a basis with explicit *electron translation factors* [20] $exp(-i\vec{v}_A \cdot \vec{r})$, where $\vec{v}_A$ is the velocity of center A, but in its full implementation this would require extension of current integral codes.

Time-independent approaches introduce nonadiabatic coupling by expanding the full wavefunction in terms of adiabatic states with each term being a product of an eigenstate of the electronic Hamiltonian and a nuclear wavefunction. The coupling terms arise from the nuclear kinetic energy operator acting on the electronic adiabatic states, which are parametrically dependent on the nuclear positions. Such coupling terms are absent when the full wavefunction is expanded in terms of diabatic states with each term being a product of an electronic state independent of nuclear coordinates and a nuclear wavefunction. Similarly, in time-dependent treatments coupling terms emerge from using electronic basis functions that depend on nuclear coordinates, and possibly also on nuclear velocities. These coupling terms are absent when the electronic basis is fixed in space, as is the case for numerical grids fixed in the lab frame. The dynamical metric matrix in Eq. (5) would in such a case have no coupling terms.

The influence of the nonadiabatic coupling terms in Eq. (5) is in many cases essential in order to describe even a qualitatively correct dynamics [21]. Neglecting the coupling terms in END generates dynamical equations identical to those used by others [22]. Other approaches that neglect electron-nuclear coupling include dynamics on a single potential energy surface and dynamics using fictitious kinetic energy terms to force the dynamics close to a surface as does the method of Car and Parrinello [4, 6, 7]. Part of the coupling effects can be handled via electron translation factors, as is done by Micha and Runge [13], but that still accounts for only part of the coupling. A dynamic treatment such as the Close Coupling method [23, 2] uses electron translation factors, but limits the dynamics to fixed trajectories, which also neglects full electron nuclear coupling terms.

Total cross sections may not be too sensitive to the neglect of electron nuclear coupling terms, but differential cross sections and details such as the presence or absence of rainbow scattering, state to state transition probabilities, branching of reaction channels, etc. cannot be predicted without accounting for the full coupling.

In Fig. 1 the electron transfer probability at 250 eV for the $H^+ + H$ system as a function of scattering angle is depicted. Results from two experiments [24, 25] are compared to the END using a pVDZ basis. Experiments have a finite angular resolution. In Ref. [24] the resolution is reported to be $\Delta\theta=0.4°$ while Ref. [25] reports $\Delta\theta=0.6°$. END calculations were averaged to reflect the finite angular resolutions of the two experiments. This was done by calculating probabilities sufficiently close together (at some points every 0.02° apart) and then averaging the probabilities inside $\pm\Delta\theta/2$ of a given angle θ. It is interesting to note that the experimental values reported in Ref. [24] are actually more consistent with an angular resolution of 1° rather than 0.4°. The results by Helbig and Everhart are in excellent agreement with END for the maxima, but the minimum value is too high. This is most likely due to some experimental problem since the oscillations should be symmetric about a probability of 0.5 [24]. Other sources of error in the experimental results are the determination of the dissociation fraction (H/H_2 in the collision region) and the calibration necessary between the different processes (elastic, charge transfer). Another problem is that as the scattering angle grows, the number of scattered particles falls very steeply. This actually shifts the minima and maxima towards larger angles, as seen in the results for Houver *et al* at angles larger than 4°. This is because more particles are measured coming from the $-\Delta\theta$ than $+\Delta\theta$ range about a given angle θ. With these considerations, one can conclude that the agreement between theory and experiment is excellent.

In Fig. 2 the END results for the same transfer probability (using perfect resolution) is compared to the results that completely neglect the electron nuclear coupling and one for which the couplings in the electronic part only (*i.e.* the first row of the metric of Eq. (5) is retained. The latter means that there is no conservation of total momentum. It is clear that the neglect of the coupling terms leads to wrong behavior with increasing scattering angle; either incorrect number of oscillations or shifted positions of the peaks.

Reactive Collisions

ENDyne calculations of total and differential cross sections of ion-atom collisions such as proton/hydrogen, proton/helium, proton/lithium, alpha/helium [9, 26, 27, 28] with rather modest Gaussian basis sets have shown excellent agreements with an abundance of experimental data.

For instance, proton/helium collisions have been studied [26] in great detail for a variety of collision energies from 500 to 5,000 eV. The classical differential cross sections for electron transfer and elastic processes are calculated using a pVDZ basis set with excellent agreement with experiment for rainbow angles. The differential elastic cross sections with a simple semiclassical correction are indistinguishable from the experimental results.

Ongoing work for small collisional systems at energies from a few to a fraction of an eV yields similarly encouraging results. Since END imposes no restrictions on the dynamics, beyond that of basis sets and wavefunction form, basically all channels accessible from given initial conditions can be studied. The analysis of processes involving ionization with one or more electron departing are just being started. Processes involving ion-molecule collisions with bond breaking and bond formation are readily accessible with END.

Proton-hydrogen molecule collisions at 30eV have been the subject of detailed experimental investigation [29] . There have been several attempts to explain the experiments using semi-classical [29, 30] and quantum descriptions of the nuclei [31, 32]. In all these approaches DIM surfaces were used. Florescu *et al* modified the surfaces to achieve quantitative agreement with experiment [30]. Preliminary results from END show that the rainbow angle is calculated more accurately than by using DIM surfaces and the approximations inherent in the Trajectory Surface Hopping (TSH) [29] and infinite order sudden approximation (IOSA) [31, 32] approaches.

Experiment puts the primary rainbow angle for charge transfer in the $p+H_2$ collision at 30eV between 6° and 7°. The TSH and quantal IOSA approach methods place it at 10° [29, 31, 32]. Preliminary END results place the primary rainbow to be near 8.5°, with new calculations lowering this result. The primary rainbow angle for elastic and vibrationally excited collisions is also observed to be between 6° and 7°. The other approaches show a shift of approximately 2.5° to larger angles, while preliminary END results show a value of 7.5° for the rainbow angle.

Table 1 shows the different channels for the proton on H_2 collision as identified by ENDyne (no differentiation among different vibrational states is made here). It is clear from these results that the assumptions made in the IOSA and the use of a DIM surface for this system are somewhat

Table 1 Product channels for various orientations and their impact parameter ranges for $H^+ + H_2$ collisions at 30eV. Θ is the angle formed between the initial velocity vector of the proton (defined as the z axis) and the H_2 axis. The initial orientation of the H_2 molecule with respect to the x-z plane is ϕ. The impact parameter b is zero at the CM of H_2 and increases along the x axis. A range of probabilities is shown for the charge transfer channel.

(Θ,ϕ)	Dissociation	Proton exchange	Charge transfer (probability)
(0,0)	-	0.0 < b< 0.3	0.3 < b (0.4-0.0)
(45,0)	0.65 < b < 1.2	0.0 < b< 0.65	1.2 < b (0.24-0.0)
(90,0)	0.0 < b< 0.6 1.1 < b< 1.35	0.6 < b< 1.1	1.4 < b (0.26-0.0)
(90,45)	0.0 < b< 0.4	-	0.4 < b (0.2-0.0)

questionable. The orientation of the system is important in defining the outcome of a collision. It is more important for small impact parameters than for large ones. Furthermore, dissociation is not accounted for in the IOSA approach.

The total breakup channels are, of course, not accessible by the close-coupling theory or any other approach using the so called impulse approximation that does not permit the nuclear arrangement of the molecule to adjust during the collision. Some channels for the smallest impact parameters correspond to nuclear transfer and should, strictly speaking not be included in the electron transfer cross section. It is almost impossible, however, to separate experimentally these processes from the transfer, since the outgoing proton or hydrogen atom have almost the same energy as the incoming proton.

Therefore it is essential to have a fully dynamical theory accounting for electron nuclear coupling as the END in order to get all accessible product channels and to interpret the experiment properly. Artificial restrictions on the electron nuclear dynamics by prescribed trajectories, by frozen nuclear configurations, by forcing the dynamics to take place on a potential energy surface, or on several surfaces with *ad hoc* hopping introduce nonphysical dynamics and errors that are hard to control.

Another system under study is the low energy collisions of H_2^+ with H_2. This system exhibits much of the complexity of a general molecular collisional system and there are no accurate potential energy surfaces available. For the few theoretical dynamics studies that have been performed on this system [33, 34] approximate potential energy surfaces are used, and the agreement with experiment is wanting. Preliminary results for END using a 1s, 2s basis for collinear initial conditions with a single impact parameter (*i.e.* assuming spherically symmetric molecular species) show good agreement with experimental total cross section for the formation of $H_3^+ + H$. Further studies are being carried out beyond these simple assumptions for the initial conditions including all channels.

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Figure Captions

Figure 1 Transfer probability versus scattering angle for p+H collision at 250 eV. END using pVDZ basis and three averaged results using an angular resolution $\pm\Delta\theta$ given in parenthesis. Experiments: Exp1: Ref. [24], Exp2: Ref [25].

Figure 2 Transfer probability versus scattering angle for p+H collision at 250 eV, using pVDZ basis. Solid line same as in Fig 1. Dotted line without any electron-nuclear coupling. Dashed line: neglecting momentum conserving couplings.

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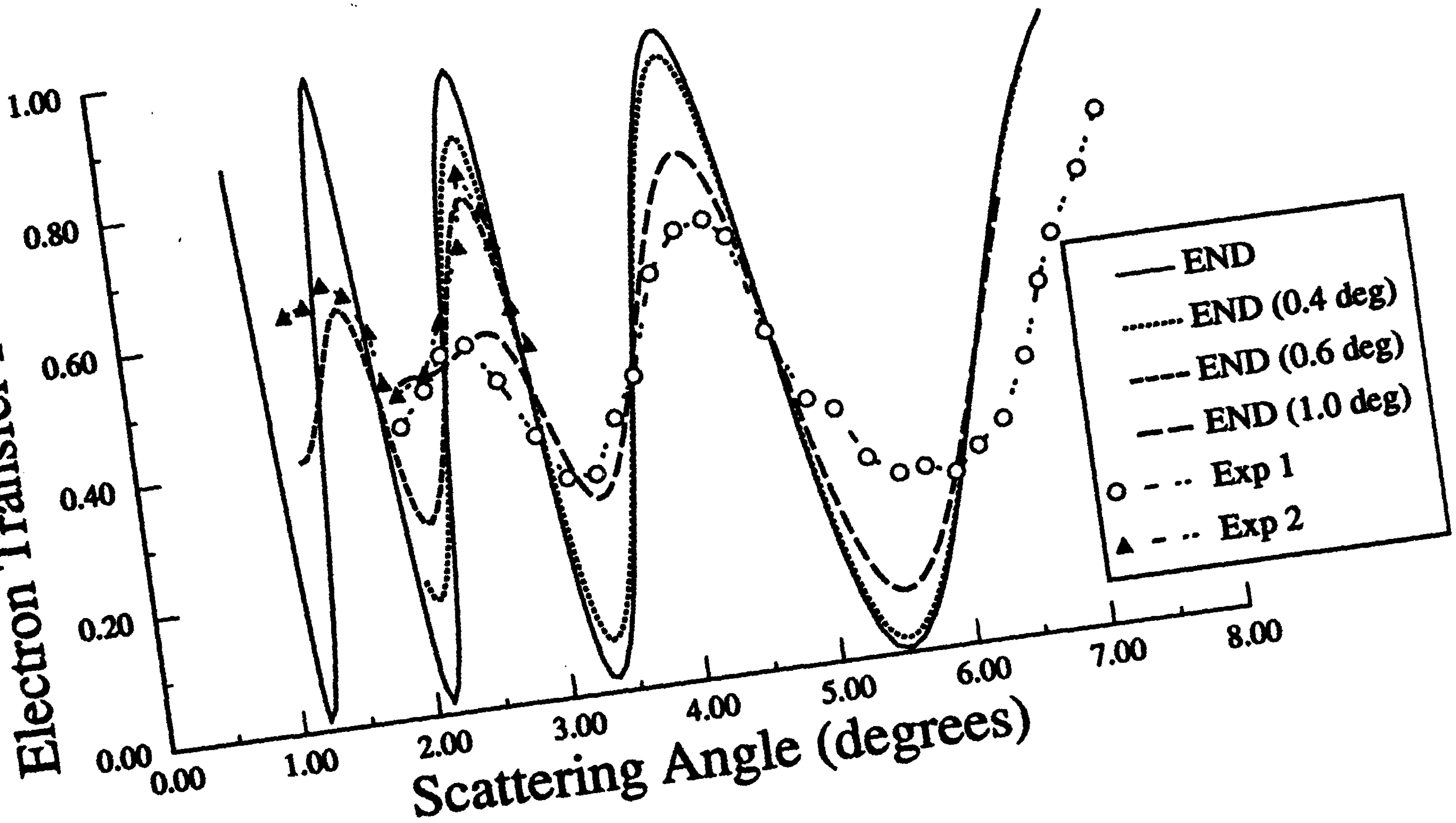

Fig. 1 Diz & Ohrn 1994

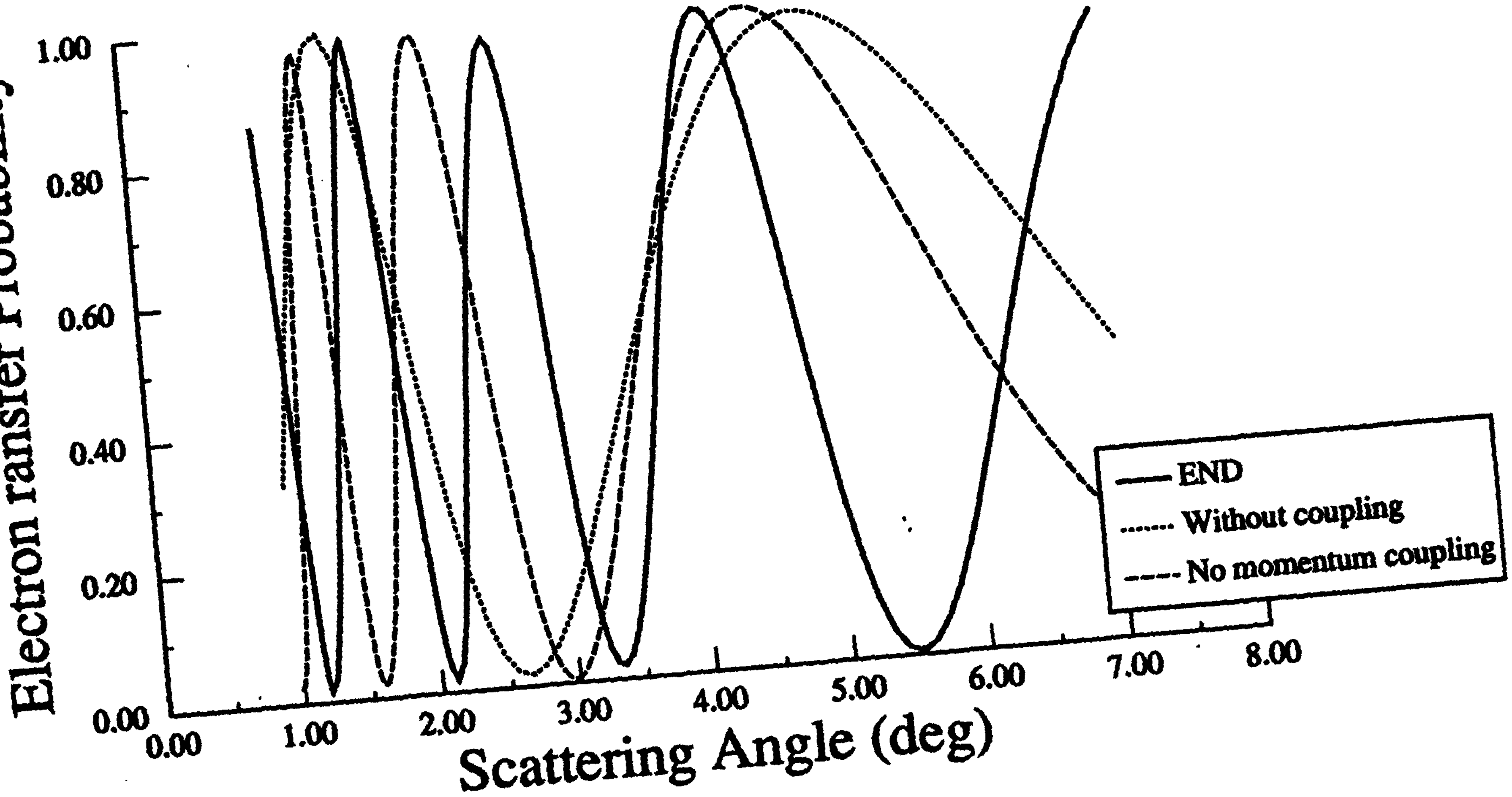

Fig. 2 Diz & Ohrn 1994