Inter-atomic contributions to high-energy electron-molecule scattering

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Abstract

We derive an accurate formula for the rotationally and vibrationally averaged three-atom term in the series expansion of the electron-molecule scattering cross-section. This formula uses the atomic scattering factors as well as the atomic scattered wavefunctions and, in addition, the spherical averaging properties of the three-atom term. The series expansion is performed numerically. The oscillations of our three-atom cross-sections tend to be in phase with those of previous calculations, but have smaller amplitudes.

1. Introduction

The total cross-section at scattering angle θ for a free molecule may be conveniently written as

$$S(\theta) = \sum_{i=1}^{\infty} J_i(0) G_i(\theta) J_i(\theta),$$

where $J_i(0)$ is the $i$th potential in isolation. These atomic scattered wavefunctions can be calculated with the usual method of partial waves.

2. Theory

Our aim, therefore, is to solve Schrödinger’s equation for a scattering potential $U$. We derive an accurate formula for the rotationally and vibrationally averaged three-atom term. The integration over $\sin \theta$ was performed numerically using 800 points between $0$ and $\pi$ (100 steps). In Fig. 2 are plots of $I_1$ at 10 keV for various hypothetical molecules of $F_2$ and $F_4$. With the exception of the linear molecule, the current results lie in between those of Kohl and Arvedson [7] and the ITP calculations of Miller and Bartell [8] but have significantly lower amplitude. The peak positions of all three methods are, however, in good agreement.

3. Multiple scattering

Once the atomic scattered wavefunctions have been determined they can be used in Eq. (2) to find the molecular wavefunction to second-order. We write the scattered wavefunction for the $i$th atom at absolute position $r$ as

$$\psi_i^s(r') = \sum_{\alpha} \psi_{i,\alpha}^s(r') \delta(r' - r_{i,\alpha}) \cdot \psi_i(r_{i,\alpha}),$$

where $\alpha$ is the position of the molecular wavefunction between the $i$th and the $i+1$th atom and $\psi_i(r_{i,\alpha})$ is the $i$th atomic scattered wavefunction. Let us use the short-hand $\alpha = a, \ldots, c$, etc. and constrain $\alpha$ to be in the $z$ direction impinging on atom $i$ ($r_i$). The total scattered wavefunction to second order may be written for a molecule of $n$ atoms as

$$\psi^s(r') = \sum_{\alpha_1, \alpha_2} \psi_{1,\alpha_1}^s(r') \psi_{2,\alpha_2}^s(r_{2,\alpha_2}) \psi_2(r_{2,\alpha_2}) \psi_1(r_{1,\alpha_1}).$$

4. Results

4.1 Single atom scattering

The atomic density is determined by self-consistently solving the density functional theory (DFT) Dirac-Kohn-Sham equations [4] for the spherically symmetric neutral atom within the local density approximation (LDA) [5]. Then the partial wave problem is solved with the potential $V(r)$ taken to be the classical electrostatic potential of the atom.

5. References


References