

Metastable States of Molecules

E. B. Davies

St. John's College, Oxford OX1 3JP, England

Abstract. We define metastable states to be density matrices which are at local minima of a certain non-linear functional, and investigate their general properties, proving in particular that the metastable states are not necessarily unique but are “modified Gibbs states”. The case of an atom in an external electric field is investigated in some detail.

1. Introduction

We consider a molecule composed of $(N + 1)$ spinless, distinguishable, three-dimensional particles in the centre of mass coordinate system. The Hamiltonian H on the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^{3N})$ is

$$H = H_0 + V(x_1, \dots, x_N), \quad (1.1)$$

where the internal kinetic energy operator H_0 of the molecule is translation invariant and satisfies

$$-\delta\Delta \leq H_0 \leq -\delta^{-1}\Delta \quad (1.2)$$

for some $\delta > 0$, and we assume that the potential V arises from pair interactions between the various particles, and has form bound zero with respect to $-\Delta$, so that (1.1), interpreted as a form sum, defines H as a semibounded self-adjoint operator.

If the set of mixed states ϱ on \mathcal{H} is defined by

$$X = \{\varrho : \varrho \geq 0 \text{ and } \text{tr}[\varrho] = 1\}$$

then the entropy of a state ϱ is

$$S(\varrho) = -\text{tr}[\varrho \log \varrho]$$

and its free energy at the inverse temperature $\beta > 0$ is

$$\text{tr}[H\varrho] - \beta^{-1}S(\varrho).$$