Pramāṇa – J. Phys., Vol. 28, No. 6, June 1987, pp. 633–639. © Printed in India.

Relativistic extension of the Hohenberg-Kohn theorem

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MS received 5 February 1987; revised 10 April 1987

Abstract. Using the configuration-space Hamiltonian H_+ which is derivable within the framework of quantum electrodynamics, we extend the Hohenberg-Kohn theorem to the relativistic theory of electrons in atoms or molecules.

Keywords. Continuum dissolution; variational collapse; Hohenberg-Kohn; relativistic.

PACS Nos **03·65; 03·70; 11·10**

1. Introduction

Many authors (Rajagopal and Callaway 1973; Rajagopal 1978; Ramana and Rajagopal 1979; MacDonald and Vosko 1979) have formulated the relativistic density functional theory (DFT) and used it to discuss simplified systems like the electron gas. They have expressed the expectation value of the (field-theoretical) Hamiltonian as a functional of the four-current (and charge) density,

$$\langle H \rangle = E_{A^{\mu}_{\text{ext}}}[J_\mu]. \tag{1}$$

The four-current (and charge) density is given by

$$J_\mu(\mathbf{r}) = e\langle :\bar{\psi}(\mathbf{r})\gamma_\mu \psi(\mathbf{r}): \rangle. \tag{2}$$

To our knowledge, all these formulations depend on the assumption that the correct J_μ minimizes $E_{A^{\mu}_{\text{ext}}}$ and yields the energy of the ground state; (of course, the minimization is subject to the conditions that $\partial^\mu J_\mu = 0$ and that the total number of electrons remains constant). In other words, it is assumed that the Hamiltonian possesses a ground state (Rajagopal 1979; see also Xing-Xu *et al* 1984). With this assumption the (non-relativistic) Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) is readily extended to the relativistic case.

Now, there are two problems connected with relativistic quantum chemical calculations using the linear expansion technique (Schwarz and Wallmeier 1982): (i) one needs a relativistic Hamiltonian which has at least a partially discrete eigenvalue spectrum, (the Dirac-Coulomb Hamiltonian suffers from continuum dissolution) and (ii) calculations based on usual relativistic Hamiltonians are not always safe from variational collapse (a term that is commonly used to describe a finite basis set effect). The first difficulty is usually waived by relying on projected Hamiltonians derived from