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Autor: Macris, N. / Martin, Ph.A. / Pulé, J.

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A Statistical Mechanical Model for Equilibrium Ionization

N. Macris* Ph. A. Martin
Institut de Physique Théorique
Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens
CH-1015 Lausanne, Switzerland

J. Pulé
Department of Mathematical Physics
University College, Belfield
Dublin 4, Ireland

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Abstract

A quantum electron interacts with a classical gas of hard spheres and is in thermal equilibrium with it. The interaction is attractive and the electron can form a bound state with the classical particles. It is rigorously shown that in a well defined low density and low temperature limit, the ionization probability for the electron tends to the value predicted by the Saha formula for thermal ionization. In this regime, the electron is found to be in a statistical mixture of a bound and a free state.

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I. Introduction

It is a problem of conceptual interest and practical importance in quantum statistical mechanics to understand how atoms and molecules can be formed. A number of different approaches have been developed in the literature, using many body and quantum field techniques as well as various types of cluster expansions, see for instance [1, 2, 3] and references quoted there. As far as rigorous results are concerned, Fefferman [4] has given a beautiful proof that in an appropriate low temperature and low density regime, electrons and protons in thermal equilibrium form a gas of hydrogen atoms in their ground state (see also [14] for a recent generalization of Fefferman results by different methods). Another situation, called ionization equilibrium, occurs when only a (macroscopic) fraction of electron-proton pairs are bound and in equilibrium with the remaining free charges. The ionization equilibrium interpolates between the purely atomic phase and a pure plasma phase where no charges are bound.

In the standard thermodynamical treatment of ionization equilibrium [5], one considers the atoms (a) the electrons (e) and the protons (p) as three different chemical species, having chemical potentials $\mu_{a'}$, $\mu_{e'}$, $\mu_{p'}$, and number densities $\rho_{a'}$, $\rho_{e'}$, ρ_{p} . If all species are assumed to behave as perfect gases (all atoms being in their ground state), one can write the law of mass action expressing the chemical equilibrium of the three species at inverse temperature $\beta = \frac{1}{k_BT}$ ($k_B = Boltzmann$ constant)

$$\frac{\rho_{\rm p} \, \rho_{\rm e}}{\rho_{\rm a}} = \left(\frac{m_{\rm e}}{2\pi \, \beta h^2}\right)^{3/2} \, {\rm e}^{-\beta Eo} \tag{1.1}$$

In (1.1), $-E_0$ ($E_0 > 0$) is the ground state energy of the atom and m_e is the mass of the electron (the proton is considered as static and the spin has been neglected). Then the fraction γ_i of ionized electrons defined by

$$\gamma_{i} = \frac{\rho_{e}}{\rho_{a} + \rho_{e}} \tag{1.2}$$

is equal to

$$\gamma_{i} = \left(1 + \rho_{p} \left(\frac{2\pi \bar{h}^{2} \beta}{m_{e}}\right)^{3/2} e^{\beta E o}\right)^{-1}$$

$$(1.3)$$

Using the neutrality $\rho_e = \rho_p$ and the law of perfect gases $P = (\rho_a + \rho_p + \rho_e)k_BT$, one can express γ_i in terms of the pressure P

$$\gamma_{i} = \left(1 + \beta P \left(\frac{2\pi \bar{h}^{2} \beta}{m_{e}}\right)^{3/2} e^{\beta E_{o}}\right)^{-1/2}$$

$$(1.4)$$

a formula called the Saha equation for thermal ionization.

The statistical mechanical formulation of the same problem is very different. Here we have only electrons and protons in a box, and no a priori distinction between "atomic" or "free" ones. Moreover, assuming overall neutrality, there is only one chemical potential μ (or activity $\zeta = e^{\beta\mu}$) conjugated to the total particle number. Then, in a grand-canonical description, the question is to find a regime of μ and β where ionization equilibrium is established. The elementary thermodynamical derivation (1.1)-(1.4) shows that the ionization equilibrium regime described by the Saha equation requires the temperature to be very small so that all atoms are in their ground states and the system to be sufficiently dilute to obey the law of perfect gases. We must therefore consider limiting situations where $\beta \to \infty$ and $\zeta = e^{\beta\mu} \to 0$ in an appropriate way.

In fact, the following picture is expected. If $\mu < -E_0$ is a fixed chemical potential strictly smaller than the atomic ground state energy and $\beta \to \infty$, the system is asymptotic to a gas of free particles. If μ is chosen slightly above $-E_0$ (i.e. $-E_0 < \mu \le -E_0 + \delta$, δ positive and small) and $\beta \to \infty$, the system behaves as a gas of non interacting atoms*. In the first case the density is lowered so fast that particles have no chance to bind, while in the second one, the density is maintained at the adequate level for a complete formation of atoms. Ionization equilibrium phases precisely occur at the borderline between these two cases, letting μ tend to $-E_0$ as $\beta \to \infty$. The actual ionized fraction is determined by the rate of convergence of μ to $-E_0$. Finally if the density is increased by taking μ larger than $-E_0 + \delta$, a variety of other low temperature phases can occur, ranging from dilute molecular gases to states of dense matter.

In this paper, we present a rigorous study of ionization equilibrium in a simplified model which has however the essential features of the general situation. We consider a single quantum mechanical particle ("the electron") in thermal equilibrium with a gas of classical particles (static "protons" or "impurities"). Each impurity is the source of an attractive short range (i.e. integrable) potential which can bind the electron. The impurities do not interact between themselves except for an hard core repulsion needed to insure stability, and the grand canonical ensemble is used. In this model the Saha coefficient γ_i is identified with the averaged ionization probability for the electron at temperature β^{-1} and chemical potential μ . Then we show that the picture described above for the formation of an atom is indeed correct. In particular, we determine the appropriate low temperature and low density limit where ionization equilibrium occurs and prove that γ_i is given by the Saha equation (1.3) in this limit. Moreover, the electron is found in a statistical mixture of a free state and a bound state, in conformity with the thermodynamical view that ionization

^{*} This is the situation considered by Fefferman in [4]

equilibrium is a phase equilibrium between two different "species", the free and the bound electron.

In section II, we give a precise formulation of the model, of the relevant class of potentials, and of the ionization probability. Then we discuss the ionization equilibrium limit and the basic mechanisms at a heuristic mathematical level. In section II we collect useful mathematical facts and state our two main propositions. The necessary mathematical background is essentially provided by the theory of Schrödinger semi-groups extensively developed in [6] by B. Simon. The only additional information needed here is a control of some of the estimates given in [6] uniformly with respect to the number and the location of the impurities. The Feynman-Kac representation of the kernels is also a convenient tool in various parts of the paper. In section III, we write down the low activity expansion of the ionization probability (or, more precisely, of its Laplace transform), and establish its convergence and its thermodynamic limit. Section IV is devoted to an analysis of these low activity series in the ionization equilibrium limit, so proving the Saha formula. The analysis relies on a specific form of the stability estimate (lower-bound) for the hamiltonian of the electron interacting with n impurities. In section VI, we show that the desired lower bound can always be satisfied for any potential in our class, with a suitable choice of the hard core diameter of the impurities. Finally, section VII presents additional aspects and concluding remarks.

II. The model and the Saha formula

As stated in the introduction, the model consists of a quantum mechanical particle of mass m (the "electron") in thermal equilibrium with a classical gas (the "impurities"). The electron interacts with each of the impurities by means of an spherically symmetric attractive potential satisfying the conditions

$$(i) V(x) \le 0 (2.1)$$

(ii) Either V(x) is continuous on \mathbb{R}^3 or V(x) is continuous on $\mathbb{R}^3 \setminus \{0\}$ with $V(x) \to -\infty$, $|x| \to 0$ and

$$\int dx |V(x)|^2 < \infty \tag{2.2}$$

$$|x| \le 1$$

(iii) There exists $\eta > 3$, R > 0 and M > 0 such that

$$|V(\mathbf{x})| \le \frac{M}{|\mathbf{x}|^{\eta}} \qquad |\mathbf{x}| \ge R \tag{2.3}$$

Note that V(x) is locally square integrable, and integrable at infinity, thus V(x) belongs to $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$.

The impurities have mass m_p and a repulsive interaction between themselves given by a spherical hard core of radius d.

If there are no impurities, the energy of the electron is purely kinetic

$$H^{0} = -\frac{\hbar^2}{2m_e}\Delta \tag{2.4}$$

where Δ is the Laplacian with domain $D(\Delta)$ in \mathcal{L}^2 (R^3). For configurations of n impurities at $r_1, \ldots, r_n, |r_i - r_j| \ge 2d, i \ne j = 1, \ldots, n$, and $n \ge 1$, the hamiltonian of the electron

$$H^{n}(\mathbf{r}_{1},...,\mathbf{r}_{n}) = -\frac{\hbar^{2}}{2m_{e}}\Delta + \sum_{j=1}^{n} V(\mathbf{r}_{j} - \mathbf{x}) = H^{o} + V^{n}(\mathbf{r}_{1},...,\mathbf{r}_{n})$$
 (2.5)

is self adjoint on $D(\Delta)$ and bounded below by the standard theorems on perturbation of the Laplacian by a square integrable potential. Moreover, it has a finite number of bound states of finite multiplicities with negative energies and an absolutly continuous spectrum on $[0, \infty]$. In particular, the one-impurity hamiltonian $H^1(r_1)$ is unitarily equivalent by translation invariance to

$$H^{1}(0) \equiv H^{1} = -\frac{\hbar^{2}}{2m_{e}}\Delta + V(x)$$
 (2.6)

which has a non degenerate ground state with energy $-E_0$ ($E_0 > 0$) and wave function $\psi_0(x)$.

For the n-impurities hamiltonians (2.5) with $n \ge 2$, we shall assume in the main body of the paper that the following stability estimate holds

$$H^{n}(\mathbf{r}_{1}, ..., \mathbf{r}_{n}) \ge -K n$$
, for $|\mathbf{r}_{i} - \mathbf{r}_{j}| \ge 2 d$, $i \ne j = 1, ..., n$, $n \ge 2$ (2.7)
 $0 \le K < E_{0}$

with some constant K independent of n and the r_j . The strict inequality $K < E_0$ means that the binding energy per impurity is the largest when the electron forms an "atom" with an single impurity. Examples of potentials and choices of d such that (2.7) is verified are given in Section VI. In fact, (2.7) will be trivially satisfied for large n since the $H^n(r_1, ..., r_n)$ will be bounded below uniformly with respect to n and the r_j .

To define the equilibrium properties of the system, we confine the electron and the classical gas in a bounded open region Λ with smooth boundaries $\partial \Lambda$. The finite volume hamiltonians $H^n_{\Lambda}(\mathbf{r}_1,...,\mathbf{r}_n)$ are defined as in (2.4) and (2.5) with Δ replaced by the Laplacian Δ_{Λ} with Dirichlet boundary conditions on $\partial \Lambda$. Then the grand canonical partition function is given by

$$\Xi_{\Lambda}(\beta, z) = \text{Tr exp}[-\beta H_{\Lambda}^{0}] +$$

$$\sum_{n=1}^{\infty} \frac{z^n}{n!} \int_{\Lambda} d\mathbf{r}_1 \dots \int_{\Lambda} d\mathbf{r}_n \operatorname{Tr} \exp \left[-\beta H_{\Lambda}^n (\mathbf{r}_1, ..., \mathbf{r}_n)\right] \chi_d(\mathbf{r}_1, ..., \mathbf{r}_n)$$
 (2.8)

where β is the inverse temperature and z the activity of the classical gas related to its chemical potential μ by

$$z = (m_p/2\pi\beta \bar{h}^2)^{3/2} e^{\beta\mu}$$
 (2.9)

In (2.8), $\chi_d(r_1, ..., r_n)$ is the hard core exclusion

$$\chi_{d}(\mathbf{r}_{1},...,\mathbf{r}_{n}) = \prod_{i < j}^{n} \chi(\mathbf{r}_{i} - \mathbf{r}_{j}) , \chi(\mathbf{r}) = \begin{cases} 1; & |\mathbf{r}| > 2d \\ & n \ge 2; \\ 0; & |\mathbf{r}| < 2d \end{cases}$$
 (2.10)

 $\chi_d(r) = 1$ and the traces are taken on $L^2(\Lambda)$.

If $A = \{A^n(r_1,...,r_n), n = 0, 1, 2, ...\}$ is an observable of the system (i.e. for each n, $A^n(r_1,...,r_n)$ is an observable of the electron depending on the configuration of the impurities $r_1,...,r_n$), the finite volume grand-canonical average of A is defined by

$$\langle A \rangle_{\Lambda}(\beta, z) = \frac{1}{\Xi_{\Lambda}(\beta z)} \left(\text{Tr } A^{o} \exp[-\beta H_{\Lambda}^{0}] + \sum_{n=1}^{\infty} \frac{z^{n}}{n!} \int_{\Lambda} d\mathbf{r}_{1} \dots \int_{\Lambda} d\mathbf{r}_{n} \right)$$

$$\text{Tr } A^{n}(\mathbf{r}_{1}, \dots, \mathbf{r}_{n}) \exp[-\beta H_{\Lambda}^{n}(\mathbf{r}_{1}, \dots, \mathbf{r}_{n})] \chi_{d}(\mathbf{r}_{1}, \dots, \mathbf{r}_{n})$$

$$(2.11)$$

We now consider the density distribution $\rho_{\Lambda}(E,\beta,z)$ of the energy of the electron in the gas at temperature β^{-1} and activity z. This quantity is formally defined by the average

$$\rho_{\Lambda}(E, \beta, z) = \langle \delta(E - H_{\Lambda}) \rangle_{\Lambda}(\beta, z)$$
 (2.12.a)

where

$$\delta(E - H_{\Lambda}) = \{\delta(E - H_{\Lambda}^{n}(r_{1},...,r_{n}))\}$$
 (2.12.b)

To make this definition mathematically correct we introduce the probability measure $\rho_{\Lambda}(.; \beta, z)$ on the real line in the following way. Let Ω be a Borel set of R and let $E_{\Lambda}^{\ n}(\Omega, r_1, ..., r_n)$ be the spectral projection of $H_{\Lambda}^{\ n}(r_1, ..., r_n)$ corresponding to the set Ω . We define $P_{\Lambda}(.; \beta, z)$ by

$$P_{\Lambda}(\Omega; \beta, z) = \langle E_{\Lambda}(\Omega) \rangle_{\Lambda}(\beta, z)$$
 (2.13)

^{*} z includes the thermal wave length of the impurities

where $E_{\Lambda}^{n}(\Omega) = \{ E_{\Lambda}^{n}(\Omega, r_{1}, ..., r_{n}) \}$. Of course formally

$$P_{\Lambda}(\Omega; \beta, z) = \int_{\Omega} dE \rho_{\Lambda}(E; \beta, z).$$

Since in infinite space, quantum states for the hamiltonian (2.5) with $E \ge 0$ (resp. E < 0) represent ionized states (resp. bound states), we define the ionization probability $\gamma_i(\beta, z)$ (resp. the binding probability $\gamma_b(\beta, z)$) by

$$\gamma_{i}(\beta, z) = \lim_{\varepsilon > 0; \varepsilon \to 0} p((-\varepsilon, \infty); \beta, z)$$
(2.14)

$$\gamma_{b}(\beta, z) = \lim_{\varepsilon > 0; \ \varepsilon \to 0} p((-\infty, -\varepsilon); \beta, z)$$
 (2.15)

where p(.; β , z) is the infinite volume limit of $p_{\Lambda}(.; \beta, z)$. It will be shown that $p_{\Lambda}(.; \beta, z)$ is also a probability measure and therefore $\gamma_i(\beta, z) + \gamma_b(\beta, z) = 1$.

In the rest of this section, we want to show on heuristic grounds that the coefficient $\gamma_i(\beta, z)$ reduces in an appropriate low density and low temperature limit to the Saha ionisation rate that has been derived in the introduction on purely thermodynamical grounds. In place of (2.12), it is more convenient to work with its Laplace transform*

$$g_{\Lambda}(\lambda, \beta, z) = \int_{-\infty}^{\infty} dE \exp[-\lambda E] p_{\Lambda}(dE; \beta, z) = \langle \exp[-\lambda H_{\Lambda}] \rangle_{\Lambda}$$
 (2.16)

with

$$\exp[-\lambda H_{\Lambda}] = \left\{ \exp\left[-\lambda H_{\Lambda}^{n}(\mathbf{r}_{1},...,\mathbf{r}_{n})\right] \right\}$$
 (2.17)

It follows from (2.11), (2.17) and (2.8) that $g_{\Lambda}(\lambda, \beta, z)$ is the ratio of two partition functions with shifted inverse temperatures

$$g_{\Lambda}(\lambda, \beta, z) = \frac{\Xi_{\Lambda}(\beta + \lambda, z)}{\Xi_{\Lambda}(\beta, z)}$$
(2.18)

Introducing the partition function $\Xi_{\Lambda}^{0}(z)$ of the classical gas

^{*} It will be shown in the next section that the support of p_{Λ} (. ; β . z) is bounded below

$$\Xi_{\Lambda}^{0}(z) = 1 + \sum_{n=1}^{\infty} \frac{z^{n}}{n!} \int_{\Lambda} d\mathbf{r}_{1} ... \int_{\Lambda} d\mathbf{r}_{n} \chi_{d}(\mathbf{r}_{1}, ..., \mathbf{r}_{n})$$
 (2.19)

we can write

$$g_{\Lambda}(\lambda, \beta, z) = \frac{f_{\Lambda}(\beta + \lambda, z)}{f_{\Lambda}(\beta, z)}$$
 (2.20)

with

$$f_{\Lambda}(\beta, z) = \frac{1}{|\Lambda|} \frac{\Xi_{\Lambda}(\beta, z)}{\Xi_{\Lambda}^{0}(z)}$$
 (2.21)

According to (2.8) and (2.19), the first terms of the low activity expansion of $f_{\Lambda}(\beta,z)$ are

$$f_{\Lambda}(\beta, z) = \frac{\text{Tr exp}[-\beta H_{\Lambda}^{0}]}{|\Lambda|} + z \frac{1}{|\Lambda|} \int_{\Lambda} d\mathbf{r}_{1} \, \text{Tr} \left(\exp[-\beta H_{\Lambda}^{1}(\mathbf{r}_{1}) - \exp[-\beta H_{\Lambda}^{0}] \right) + 0 \, (z^{2})$$
 (2.22)

In the infinite volume limit, we have

$$\lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \operatorname{Tr} \exp[-\beta H_{\Lambda}^{0}] = \left(\frac{m_{e}}{2\pi \beta \bar{h}^{2}}\right)^{3/2}$$
 (2.23)

and

$$\lim_{|\Lambda| \to \infty} \operatorname{Tr} \left(\exp[-\beta H_{\Lambda}^{1}(r_{1})] - \exp[-\beta H_{\Lambda}^{0}] \right) = \operatorname{Tr} \left(\exp[-\beta H^{1}] - \exp[-\beta H^{0}] \right) (2.24)$$

which is independent of r_1 by the unitary equivalence of $H^1(r_1)$ and H^1 . Thus, we find (taking the infinite volume limit term by term in (2.22))

$$\lim_{|\Lambda| \to \infty} f_{\Lambda}(\beta, z) = f(\beta, z)$$

$$= \left(\frac{m_e}{2\pi\beta \bar{h}^2}\right)^{3/2} + z \operatorname{Tr}(\exp[-\beta H^1] - \exp[-\beta H^0]) + O(z^2)$$
(2.25)

Now, let $z \to 0$, $\beta \to \infty$, or equivalently $\mu \to -E_0$, $\beta \to \infty$ in such a way that

$$z\left(\frac{2\pi\beta\hbar^2}{m_e}\right)^{3/2}\exp(\beta E_o) = \left(\frac{m_p}{m_e}\right)^{3/2}\exp\left[\beta\left(\mu + E_o\right)\right] \to w$$
 (2.26)

where w is some number, $0 \le w < \infty$. Since for β large

$$\operatorname{Tr}\left(\exp[-(\beta+\lambda)H^{1}]-\exp[-(\beta+\lambda)H^{0}]\right) = \exp[(\beta+\lambda)E_{o}] + o\left(\exp[(\beta+\lambda)E_{o}]\right) \ (2.27)$$

we get from (2.25) and (2.27) in the scaling limit (2.26)

$$\lim_{\beta \to \infty} \left(\frac{2\pi \beta \hbar^2}{m_e} \right)^{\beta/2} f(\beta + \lambda, z) = 1 + w \exp[\lambda E_o]$$
 (2.28)

and thus from (2.20)

$$\lim_{\beta \to \infty} g(\lambda, \beta, z) = \frac{1 + w \exp[\lambda E_0]}{1 + w}$$
 (2.29)

provided that the terms of order larger or equal to two in (2.25) vanish in this limit. Since $g(\lambda, \beta, z)$ is the Laplace transform of the energy probability density $\rho(E, \beta, z)$, (2.29) implies that this density converges to

$$\lim_{\beta \to \infty} \rho(E, \beta, z) = \frac{1}{1+w} \delta(E) + \frac{w}{1+w} \delta(E+E_0)$$
 (2.30)

and hence that the ionisation probability (2.14) tends to

$$\lim_{\beta \to \infty} \gamma_i(\beta, z) = \gamma_i = \frac{1}{1+w}$$
 (2.31)

Recalling the definition (2.26) of w and noting that as $z \to 0$, z becomes equal to ρ , the density of the gas, we see that γ_i can be identified to the Saha coefficient (1.3).

If $\mu \to -E_0$ and $\beta \to \infty$ in such a way that the limit (2.26) is equal to zero, one finds $\gamma_i = 1$ so the electron is ionized with probability one. Obviously the same result is true if μ is any fixed chemical potential in the range $-\infty < \mu < -E_0$. On the other hand, if the quantity (2.26) diverges as $\mu \to -E_0$ and $\beta \to \infty$, one obtains from (2.20) with $w = \infty$, $\lim_{n \to \infty} g(\lambda, \beta, z) = \exp(\lambda E_0)$ and so $\gamma_i = 0$: the atom is formed with probability one. Moreover, the pure atomic phase is also obtained in the whole range $-E_0 < \mu \le -K$. Indeed, $g(\lambda, \beta, z)$ is the ratio of the two low activity series $f(\beta + \lambda, z) = \sum_n z^n f^n(\beta + \lambda)$ and $f(\beta, z) = \sum_n z^n f^n(\beta)$. Since $f^n(\beta)$ involves linear

combinations of Tr $\exp\left[-\beta H^k(r_1,\ldots,r_k)\right]$, $k=0,\ldots,n$ (see section IV) the asymptotic behaviours of the n^{th} order terms of these series are expected to be of the form (up to algebraic functions of β)

$$\begin{split} z^n \ f^n(\beta + \lambda) &\sim \left(\frac{m_p}{2\pi\beta h^2}\right)^{3n/2} \exp\left[\beta(E^n + \mu n)\right] \exp(\lambda \, E^n) \\ z^n \ f^n(\beta) &\sim \left(\frac{m_p}{2\pi\beta h^2}\right)^{3n/2} \exp\left[\beta(E^n + \mu n)\right] \end{split} \tag{2.32}$$

with $E^n = -\inf_{r_1; ...; r_n \mid r_i - r_i| \ge 2 d} H^n(r_1, ..., r_n)$ and $E^1 \equiv E_0$.

One readily verifies that the inequality (2.7) (i.e. $E^n \le Kn$, $0 < K < E_o$, $n \ge 2$) together with $-E_o < \mu \le -K$ implies

$$E^{1} + \mu > 0$$
, $E^{n} + \mu n \le 0$, $n \ge 2$ (2.33)

Thus, all the terms of series remain bounded except for the first order which diverges as $\beta \to \infty$. One concludes from (2.32) that the ratio $g(\lambda, \beta, z)$ of the two series tends to $\exp[\lambda E_0]$ and hence $\gamma = 0$.

We conclude this section with an important remark. It is essential to have are pulsive interaction between the impurities in order to find a value of μ such that inequalities of the type (2.33) hold. In orther words if the gas of impurities is a free one, it is impossible to fix the chemical potential such that the Boltzmann weight of some finite aggregate is dominant when $\beta \to \infty$. Indeed for a free gaz of impurities, E^n is a convex function of n. To show this fact we set d=0 in the definition of E^n and proceed as follows. Define the function

$$F(\lambda) = -\inf_{r_1; ...; r_{n-1}} \inf \operatorname{spec} \left[-\frac{\hbar^2}{2m_e} \Delta + \lambda V(x) + \sum_{j=1}^{n-1} V(r_j - x) \right]$$
 (2.34)

We note that $F(\lambda)$ is a convex function of λ and $F(0) = E^{n-1}$, $F(1) = E^n$. Moreover

$$E^{n+1} = -\inf_{r; r_1; ...; r_{n-1}} \inf \operatorname{spec} \left[-\frac{\overline{h}^2}{2m_e} \Delta + V(x) + V(x-r) + \sum_{j=1}^{n-1} V(r_j - x) \right]$$

$$\geq -\inf_{r_1; ...; r_{n-1}} \inf \operatorname{spec} \left[-\frac{\overline{h}^2}{2m_e} \Delta + 2V(x) + \sum_{j=1}^{n-1} V(r_j - x) \right] = F(2)$$
(2.35)

By the convexity of F we have $F(1) \leq \frac{1}{2} F(0) + \frac{1}{2} F(2)$, thus from (2.35) we get $E^n < \frac{1}{2} E^{n-1} + \frac{1}{2} E^{n+1}$, wich means that E^n is a convex function of n when d=0.

The rest of the paper is essentially devoted to the proof of the facts outlined in this section.

III. Mathematical preliminaries and statement of results

To abbreviate the notation, we set $\bar{h} = 1$, m = 1 and

$$H^{n}(r_{1},...,r_{n}) \equiv H^{n} = -\frac{1}{2}\Delta + V^{n} \text{ with } V^{n}(x) = \sum_{j=1}^{n} V(r_{j} - x).$$

For a given configuration $\mathbf{r}_1,...,\mathbf{r}_n$, V^n has at most n square integrable singularities satisfying the condition (2.2) at $\mathbf{r}_1,...,\mathbf{r}_n$, and V^n obeys (2.3) with R sufficiently large (depending on $\mathbf{r}_1,...,\mathbf{r}_n$). As already noted, $V^n(x) \in L^2(\mathbb{R}^3)$ and thus H^n (resp H^n_Λ) is self adjoint on $D(\Delta)$ (resp $D(\Delta_\Lambda)$) with form domain $D_f(\Delta)$ (resp $D_f(\Delta_\Lambda)$) where Δ_Λ is the Laplacian with Dirichlet boundary conditions [7]. Moreover, the H^n_Λ verify the same stability condition (2.7).

We shall extensively use the theory of Schrödinger semi-groups reviewed in [6], for which the natural class of potentials V is the class K₃ defined by the condition

$$\lim_{\delta \to 0} \sup_{\mathbf{x}} \int_{|\mathbf{x} - \mathbf{y}| \le \delta} \frac{|V(\mathbf{y})|}{|\mathbf{x} - \mathbf{y}|} = 0$$
(3.1)

It follows immediatly from (2.2) and (2.3) that

$$\sup_{\mathbf{x}} \int_{|\mathbf{x}-\mathbf{y}| \le 1}^{\mathrm{d}\mathbf{y}} |V^{\mathbf{n}}(\mathbf{y})|^2 < \infty \tag{3.2}$$

and this implies by the formula (A.21) of [6] that V^n belong to K_3 for each n and each configuration of impurities $r_1,...,r_n$. Hence we know that the semi-group $\exp[-tH^n]$ is an integral operator with jointly continuous uniformly bounded kernel (x | $\exp[-tH^n]$ | y) (Theorem B. 7.1 of [6]). The Feynman-Kac representation of this kernel

$$(x \mid \exp(-tH^n) \mid y) = \int d\mu \underset{x \mid 0; y \mid t}{(\omega)} \exp\left(-\int_0^t ds \mid V^n \mid \underline{\omega}(s)\right)$$
(3.3)

holds for all $x, y \in \mathbb{R}^3$, where $d\mu_{x \ 0; \ y \ t}(\underline{\omega})$ is the conditional Wiener measure for three dimensional Brownian paths $\underline{\omega}(s)$, $0 \le s \le t$ and $\underline{\omega}(0) = 0$, $\underline{\omega}(t) = x$. It is well known that the formula (3.3) is true for continuous bounded potentials

[6, 8]. Its extension to potentials having singularities of the type (2.2) is given in Appendix A. For the diagonal part of the kernel we write simply

$$(x \mid \exp(-tH^n) \mid x) = \int d\mu_{x \mid t}(\underline{\omega}) \exp \left(-\int_0^t ds \; V^n(\underline{\omega}(s)) \right)$$
(3.4)

$$= \int d\mu_{t}(\omega) \exp \left(-\int_{0}^{t} ds \, V^{n} \left(x + \underline{\omega}(s)\right)\right)$$
 (3.5)

with $d\mu_{x\,t}(\underline{\omega})=d\mu_{x\,0;\,x\,t}(\underline{\omega})$ the conditional Wiener measure for closed paths such that $\underline{\omega}(0)=\underline{\omega}(t)=x$ and $d\mu_{t}(\underline{\omega})=d\mu_{x\,=\,0;\,t}(\underline{\omega})$. For the finite volume hamiltonians $H_{\Lambda}^{\ n}$ with Dirichlet boundary conditions, one has the same formula (3.4) with $d\mu_{x\,t}(\underline{\omega})$ replaced by $d\mu_{x\,t}^{\Lambda}(\underline{\omega})$, x in Λ , where $d\mu_{x\,t}^{\Lambda}(\underline{\omega})$ is the conditional Wiener measure restricted to the set

$$\Gamma_{\Lambda}^{t} = \{ \underline{\omega}(s) \mid \underline{\omega}(s) \in \Lambda, \ 0 \le s \le t \}$$
 (3.6)

of paths that do not leave Λ (see Appendix A).

Since V^n has a finite number of square integrable singularities, the condition (2.3) implies that for j large enough, $j \in Z^3$,

$$\left(\int_{\Delta_{\mathbf{j}}} dx |V^{\mathbf{n}}(x)|^{2}\right)^{1/2} \leq \frac{M_{\mathbf{0}}}{\eta}$$

$$(3.7)$$

where Δ_j is the unit cube centered at j and M_0 an appropriate constant. Hence, by (2.2) V^n belongs to the Birman-Solomjak class, that is

$$\sum_{\mathbf{j} \in \mathbb{Z}^3} \left(\int_{\Delta_{\mathbf{j}}} \mathrm{d}x \, |V^{\mathbf{n}}(x)|^2 \right)^{1/2} < \infty \tag{3.8}$$

Therefore exp $[-\beta H^n]$ – exp $[-\beta H^0]$ is trace-class for all $\beta > 0$ [6], and since the kernels are continuous, one has

$$Tr(\exp[-\beta H^{n}] - \exp[-\beta H^{0}]) = \int dx ((x | \exp[-\beta H^{n}] | x) - (x | \exp[-\beta H^{0}] | x))$$
(3.9)

Obviously, for finite volume, $\text{exp}[-\beta\; H_{\Lambda}^{\,n}\,]$ is also trace-class and

Tr exp[
$$-\beta H_{\Lambda}^{n}$$
] = $\int_{\Lambda} dx (x | exp[-\beta H_{\Lambda}^{n}] | x)$ (3.10)

We now state the main propositions that are proven in Section IV and V. The assumptions are that V(x) verifies (2.1) - (2.3), the impurities have an hard core of radius d, and the stability condition (2.7) holds.

Proposition 1

The low activity expansion of $f_{\Lambda}(\beta, z)$ defined in (2.21)

$$f_{\Lambda}(\beta, z) = \frac{1}{|\Lambda|} \operatorname{Tr} \exp(-\beta H_{\Lambda}^{o}) + \sum_{n=1}^{\infty} z^{n} f_{\Lambda}^{n}(\beta)$$
 (3.11)

converges for |z| small enough. Moreover, its infinite volume limit exists and is given by the series

$$f(\beta, z) = \lim_{|\Lambda| \to \infty} f_{\Lambda}(\beta, z) = \left(\frac{1}{2\pi\beta}\right)^{3/2} + \sum_{n=1}^{\infty} z^n f^n(\beta)$$
 (3.12)

where the $f^n(\beta) = \lim_{|\Lambda| \to \infty} f^n_{\Lambda}(\beta)$, $n \ge 1$, are defined in Section IV by (4.37) and (4.39).

Notice that (3.12) implies the existence of the limit of the Laplace transforms (2.16)

$$\lim_{|\Lambda| \to \infty} g_{\Lambda}(\lambda, \beta, z) = g_{\Lambda}(\lambda, \beta, z) = \frac{f(\beta + \lambda, z)}{f(\beta, z)}$$

which in turn entails the convergence of the corresponding measures $p_{\Lambda}(.; \beta, z)$ to $p(.; \beta, z)$ [12].

To formulate the low density and temperature limit (2.26) we set

$$z(\beta) = \frac{w(\beta) \exp[-\beta E_0]}{(2\pi \beta)^{3/2}}$$
(3.13)

where $w(\beta)$ is some positive function of β .

Proposition 2

Assume that $\lim_{\beta \to \infty} w(\beta) = w$, $0 \le w < \infty$. Then

$$\lim_{\beta \to \infty} (2\pi \beta)^{3/2} f(\beta + \lambda, z(\beta)) = 1 + w \exp[\lambda E_0]$$
(3.14)

and the ionisation probability (2.14) tends to

$$\gamma_{i} = \lim_{\beta \to \infty} \gamma_{i}(\beta, z(\beta)) = \frac{1}{1+w}$$
(3.15)

If $w(\beta) \to \infty$ as $\beta \to \infty$ with $w(\beta) = O(\exp\beta(E_0 - K))$, the ionisation probability γ_i vanishes.

The main tool which will be used in the proofs of these propositions is a pointwise bound of the kernel $(x \mid \exp[-\beta H^n] \mid y)$ is terms of the free kernel which is uniform with respect to the number n and the locations $r_1,...,r_n$ of the impurities.

Lemma 1

There exists positive constants A and B independent of n and of $r_1,...,r_n$, $n=1,2,..., |r_i-r_i| \ge 2$ d, such that

$$(x | \exp(-tH^n)) | y) \le A e^{Bt} (x | \exp(-2tH^0) | y)$$
 (3.16)

Proof

One knows that V belongs to the class K_3 if and only if (Prop. A. 2.6 of [6])

$$v(t) = \sup_{X} \int dy \, Q_t(x - y) \, | \, V(y) \, | \, \to 0, \, t \to 0$$
 (3.17)

with

$$Q_{t}(x) = \int_{0}^{t} ds \frac{\exp(-\frac{|x|^{2}}{2s})}{(2\pi s)^{3/2}}$$
(3.18)

Choosing t_0 small enough such that $v(t_0) = v_0 < \frac{1}{4'}$ the result of the theorem (B.1.1) of [6] gives that exp-t(Ho + 2V) considered as integral operator from $\mathcal{L}^1(\ |\mathbb{R}^3)$ to \mathcal{L}^∞ is bounded with

$$\|\exp(-t(H^{o} + 2V)) f\|_{\infty} \le \frac{C \exp Dt}{(\pi t)^{3/4}} \|f\|_{1}$$
 (3.19)

$$C = \frac{1}{1 - 4 v_0} > 1$$
, $D = \frac{1}{2t_0} \ln C > 0$ (3.20)

Moreover, repeating the proof of the proposition (B.6.7) of [6], the Schwartz inequality applied to the Feynman-Kac formula for $(\exp(-tH)f)(x)$ with $H = H^0 + V$ implies

$$|(e^{-tH}f)(x)| \le [(e^{-t(H^{O}+2V)}|f|)(x)]^{1/2} [e^{-tH^{O}}|f|)(x)]^{1/2}$$
 (3.21)

$$|(e^{-tH} f)(x)| \le C^{1/2} \exp \frac{D_t}{2} \|f\|_1 \left[\frac{1}{(\pi t)^{3/2}} (e^{-tH^0} |f|)(x) \right]^{1/2}$$
 (3.22)

Letting f approach a δ at y function with $\|f\|_1 = 1$ and using the explicit form of the free kernel

$$(x \mid e^{-tH^0} \mid y) = \frac{1}{(2\pi t)^{3/2}} \exp\left(-\frac{|x-y|^2}{2t}\right)$$
 (3.23)

leads to the estimate

$$(x|e^{-tH}|y) \le A e^{Bt} (x|e^{-2tH^0}|y)$$
 (3.24)

with $A = 2^{9/4} C^{1/2}$ and $B = \frac{1}{2}D$. It is clear from (3.20) that these constants depend only on v_0 and t_0 . The lemma will be proven if v_0 can be chosen independently of the number and the location of the impurities, i.e. if , v(t) tends to zero uniformly with respect to $r_1, \dots, r_{n'}$ $n = 1, 2, \dots$

For this, we first note that

$$Q_{t}(x) = \frac{1}{(2\pi)^{3/2}} \frac{1}{|x|} \int_{\frac{|x|^{2}}{t}}^{\infty} du \frac{e^{-u/2}}{\sqrt{u}} \le \frac{C}{|x|} \exp\left(-\frac{|x|^{2}}{4t}\right)$$
(3.25)

where the first equality follows from the change of variable $s = |x|^2/u$ in (3.18). Thus one has

$$v(t) \le C \left(\sup_{x} v_1(x, t) + \sup_{x} v_2(x, t) \right)$$
 (3.26)

with

$$v_1(x, t) = \int_{|x-y| \le t^{1/4}} dy \frac{|V(y)|}{|x-y|}$$
 (3.27)

$$v_{2}(x, t) = \int_{|x-y| \ge t^{1/4}} dy \frac{|V(y)|}{|x-y|} \exp\left(-\frac{|x-y|^{2}}{4t}\right)$$
(3.28)

We estimate $v_1(x, t)$ and $v_2(x, t)$ when $V(x) = V^n(x) = \sum_{i=1}^n V(r_i - x)$.

Let B(x, a) be the ball of radius a centered at x, and R the number occurring in the condition (2.3). Then, we have

$$v_1(x, t) \le v_1^{in}(x, t) + v_1^{out}(x, t)$$
 (3.29)

with

$$v_1 {in \choose out} = \sum_{i} {in \choose out} \int_{|\mathbf{x}-\mathbf{y}| \le t^{1/4}} d\mathbf{y} \frac{|V(\mathbf{r}_i - \mathbf{y})|}{|\mathbf{x} - \mathbf{y}|}$$
(3.30)

where the summation $\sum_{i}^{\text{(in)}} \left(\text{resp} \sum_{i}^{\text{(out)}} \right)$ runs on all impurities with r_i in B (x, R + t^{1/4}) (resp outside of B(x, R + t^{1/4})).

Since $V \in K_3$, one gets for any $\varepsilon > 0$

$$\int dy \frac{|V(r_i - y)|}{|x - y|} \le \sup_{x} \int dy \frac{|V(y)|}{|x - y|} \le \varepsilon$$

$$|x - y| \le t^{1/4}$$
(3.31)

provided that $t \le t_0$, t_0 small enough and independent of r_i (see (3.1)). Hence, using the hard core condition, we find

$$v_1^{\text{in}}(x,t) \le \varepsilon \cdot \left(\text{number of impurities in B}(x,R+t_o^{1/4})\right)$$

$$\le \varepsilon \left(\frac{R+t_o^{1/4}}{d}\right)^3 \tag{3.32}$$

If r_i does not belong to $B(x, R + t^{1/4})$, we have obviously $|y-r_i| > R$ and we can apply (2.3)

$$v_1^{\text{out}}(x, t) \le \int_{|x-y| \le t^{1/4}} dy \frac{1}{|x-y|} \sum_i^{\text{(out)}} \frac{M}{|y-r_i|^{\eta}}$$
 (3.33)

The summation (3.33) is performed on the impurities located in the successive shells $\Gamma_{\rm m}=B(x,R+t^{1/4}+md)\setminus B(x,R+t^{1/4}+(m-1)d)$. If ${\bf r_i}$ is in $\Gamma_{\rm m}$ and $|x-y|\leq t^{1/4}$ (t small enough) one has

$$|y-r_i| \ge |x-r_i| - |x-y| \ge R + (m-1) d$$
 (3.34)

Using again the hard core condition to bound the number of impurities in the shell $\Gamma_{\rm m}$ the sum in (3.33) is certainly less than

$$K_{t} = \sum_{m=1}^{\infty} \left(\frac{(R + t^{1/4} + m d)^{3} - (R + t^{1/4} + (m-1)d)^{3}}{d^{3}} \right) \frac{M}{(R + (m-1)d)^{\eta}}$$
(3.35)

where K_t is finite $(\eta > 3, 0 \le t \le t_0)$, and independent of y and $r_1, ..., r_n$. Therefore, one gets

$$v_1^{\text{out}}(x, t) \le K_t \sup_{|x-y| \le t^{1/4}} \int dy \frac{1}{|y|} = 2 \pi \sqrt{t} K_t$$
 (3.36)

We can estimate $v_2(x, t)$ from (3.28)

$$v_{2}(x,t) \leq t^{-1/4} \exp\left(-\frac{1}{8t^{1/2}}\right) \int_{|x-y| \geq t^{1/4}} dy |V^{n}(y)| \exp\left(-\frac{|x-y|^{2}}{8t}\right)$$

$$\leq t^{-1/4} \exp\left(-\frac{1}{8t^{1/2}}\right) \int dy |V^{n}(y)| \exp\left(-|x-y|^{2}\right) , \quad t \leq 1/8$$

$$\leq t^{-1/4} \exp\left(-\frac{1}{8t^{1/2}}\right) \sum_{i=1}^{n} |\tilde{V}(\mathbf{r}_{i}-\mathbf{x})| \tag{3.37}$$

with

$$\widetilde{V}(x) = \int dy \exp(-|x-y|^2) |V(y)|$$
(3.38)

Clearly $|\tilde{V}(x)| \le \|V\|_1$, and it is easily verified that the convolution (3.38) of V(x) with a Gaussian satisfies the same condition (2.3) with some modified constants \tilde{R} and \tilde{M} . We perform the summation in (3.37) by first taking the impurities in the sphere $B(x, \tilde{R})$ with $|\tilde{V}(r_i - x)| \le \|V\|_1$, and then summing on the shells $B(x, \tilde{R} + m d) \setminus B(x, \tilde{R} + (m-1)d)$ where $|\tilde{V}(r_i - x)| \le \frac{\tilde{M}}{|x - r_i|^{\eta}}$ in the same way as in (3.34). Taking the hard core condition into account, this leads to

$$\sum_{i=1}^{n} |\widetilde{V}(\mathbf{r}_{i} - \mathbf{x})| \le \left(\frac{\widetilde{R}}{d}\right)^{3} \|V\|_{1} + \widetilde{K}_{o}$$
(3.39)

where \widetilde{K}_0 is the constant (3.35) with \widetilde{R} and \widetilde{M} replacing R and M and t = 0. This bound together with (3.37) shows that $v_2(x, t)$ tends to zero uniformly with respect to x and the r_i as t \rightarrow 0. By (3.32) and (3.36), the same is true for $v_1(x, t)$, and thus for v(t) by (3.26). This concludes the proof of the lemma.

As a corollary of the lemma, one obtains that binding energies

$$E^{n} = -\inf_{\mathbf{r}_{1}; ...; \mathbf{r}_{n}} \inf_{|\mathbf{r}_{i} - \mathbf{r}_{i}| \ge 2 d} H^{n}(\mathbf{r}_{1}, ..., \mathbf{r}_{n}) > 0$$
(3.40)

have a limit as $n \to \infty$.

Corollary

The binding energies En form an increasing sequence and

$$\lim_{n \to \infty} E^n = E_* < \infty \tag{3.41}$$

Proof

Since the electron-impurity potential V is negative, one has $H^{n+1} \leq H^n$, implying $E^{n+1} \geq E^n$. Let $\|\exp[-tH^n]\|_{p,p}$ be the norm of $\exp(-tH^n)$ as an operator from $\mathcal{L}^p(|\mathbb{R}^3)$ to $\mathcal{L}^p(|\mathbb{R}^3)$. The result of the lemma shows that

$$\|\exp(-tH^n)\|_{\infty,\infty} \le \sup_{x} \int dy |(x| \exp(-tH^n)|y) \le A e^{Bt}$$
 (3.42)

Furthermore, one has (theorem B. 5.1 of [6])

$$\exp(-t \inf \operatorname{spec} H^n) = \| \exp(-tH^n) \|_{2,2} \le \| \exp(-tH^n) \|_{\infty,\infty}$$
 (3.43)

hence the sequence of binding energies is bounded,

$$E^{n} \le B \tag{3.44}$$

and thus $\lim_{n\to\infty} E^n = E_* \text{ exists.}$

Clearly, $E^n \leq E_*$ implies that the stability condition (2.7) certainly holds for n large enough. One has necessarily $E_* \geq E_o$. If one would know that $E_* < 2E_o$, the inequality (2.7) would obviously hold for all $n \geq 2$ and $K = \frac{E_*}{2}$. It turns out that the estimate (3.44) of the E^n and E_* in term of B is far from being optimal (B is in general much larger than E_o ; see the remarks at the end of section VI). In section

VI, we give an estimate of E_* by another technique yielding a stability constant $K < E_0$ provided that the hard core radius is large enough.

Finally, we note that if one considers $H^0 + qV^n$ with a coupling constant $q \ne 1$, the result of the lemma as well as (3.44) are still true, and the constants A and B can be chosen independent of q for q in a neighborhood of 1.

IV. The low activity expansion

IV.1. Formal low activity series

We first calculate the coefficients $f_{\Lambda}^{n}(\beta,z)$ of the low activity expansion (3.12). Introducing the functional integral representation (3.4) for finite volume Λ and using (3.10) and (2.21), we can write

$$f_{\Lambda}(\beta,z) = \frac{1}{|\Lambda|} \int_{\Lambda} dx \int_{\Lambda}$$

where

$$\Xi(\beta, z; \omega) = 1 + \sum_{n=1}^{\infty} \frac{z^n}{n!} \int_{\Lambda} d\mathbf{r}_1 ... \int_{\Lambda} d\mathbf{r}_n \, \chi_d(\mathbf{r}_1, ..., \mathbf{r}_n) \prod_{j=1}^{n} \exp\left[-V(\mathbf{r}_j, \underline{\omega})\right]$$
(4.2)

is the classical partition function in the external (β-dependent) potential

$$V(\mathbf{r}; \omega) = \int_{0}^{\beta} ds \ V(\mathbf{r} - \underline{\omega}(s))$$
 (4.3)

To expand the integrand of (4.1), one introduces the abbreviated notation

$$\Xi(\beta, z; \omega) = 1 + \sum_{n=1}^{\infty} \frac{z^n}{n!} \int_{\Lambda} d1...dn \chi_d(1, ..., n) \prod_{j=1}^{n} f_j$$
 (4.4)

$$\Xi_{0}(z) = 1 + \sum_{n=1}^{\infty} \frac{z^{n}}{n!} \int_{\Lambda} d1...dn \chi_{d}(1,...,n)$$
 (4.5)

with $\chi_d(1, ..., n) = \chi_d(r_1, ..., r_n)$ $(\chi_d(1) = 1)$ and

$$f_{j} = \exp\left(-V(\mathbf{r}_{j}, \underline{\omega})\right)$$
 (4.6)

Then the ratio of the partition functions (4.4) and (4.5) has the expansion (see Appendix B)

$$\frac{\Xi_{\Lambda}(\beta z; \omega)}{\Xi_{\Lambda}^{0}(z)} = 1 + \sum_{n=1}^{\infty} \frac{z^{n}}{n!} a_{n}$$
 (4.7)

$$a_{n} = 1 + \sum_{k=1}^{n} \frac{n!}{k!(n-k)!} \int_{\Lambda} d1...dn \chi_{d}^{T}(1,...,k|k+1|...|n) \prod_{j=1}^{k} (f_{j}-1)$$
(4.8)

In (4.8), $\chi_d^T(1,...,k \mid k+1 \mid ... \mid n)$ is the hard core exclusion (2.10) truncated with respect to the subsets

$$q_k = \{1 ... k\}, q_{k+1} = \{k+1\}, ..., q_n = \{n\}$$

and

$$\chi_d^T(1,...,n) = \chi_d(1,...,n) , \chi_d^T(1) = 1.$$

One can write (2.10) in the form

$$\chi_{\mathbf{d}}(1,...,n) = \chi_{\mathbf{d}}(1,...,k) \prod_{k \le l < m}^{n} \chi_{\mathbf{q}_{l} \mathbf{q}_{m'}} n \ge 2$$
 (4.9)

with

$$\chi_{q_l q_m} = \prod_{i \in q_i} \prod_{j \in q_m} \chi(r_i - r_j)$$
(4.10)

Therefore, according to the Mayer connected graphs formula, one has

$$\chi_{\mathbf{d}}^{\mathbf{T}}(1,...,k \mid k+1 \mid ... \mid n) = \chi_{\mathbf{d}}(1,...,k \mid k+1 \mid ... \mid n)$$
 (4.11)

$$S(1,...,k \mid k+1 \mid ... \mid n) = \sum_{G} \prod_{(l,m) \in G} (\chi_{q_l q_m} - 1)$$
(4.12)

where the sum runs over all connected graphs G with vertices k, k+1,..., n, (S(1,...,n) = 1). Thus taking (4.8), (4.6) and (4.11) into account, we find that the coefficients $f_{\Lambda}^{n}(\beta, z)$ of the low activity expansion (3.12) have the form

$$f_{\Lambda}^{n}(\beta) = \sum_{k=1}^{n} \frac{1}{k!(n-k)!} I_{nk}^{\Lambda}, n \ge 1$$
 (4.13)

with

$$I_{nk}^{\Lambda} = \frac{1}{|\Lambda|} \int_{\Lambda} dx \ h_{nk}^{\Lambda}(x) \tag{4.14}$$

$$h_{n k}^{\Lambda}(\mathbf{x}) = \int_{\Lambda} d\mathbf{r}_{1} ... d\mathbf{r}_{n} \int d\mu_{\mathbf{x} \beta}^{\Lambda}(\underline{\omega}).$$

$$\chi_{d}(\mathbf{r}_{1},...,\mathbf{r}_{k}) S(\mathbf{r}_{1},...,\mathbf{r}_{k} | \mathbf{r}_{k+1} | ... | \mathbf{r}_{n}) \prod_{j=1}^{k} \left(\exp(-\beta V(\mathbf{r}_{j} - \underline{\omega})) - 1 \right) \quad (4.15)$$

In deriving (4.13), we have freely exchanged sums and integrals. This will be justified by the bounds obtained in the next subsection.

IV.2. Uniform bounds

We give bounds on the coefficients $I_{n\,k}^{\Lambda}$ (4.14) that are uniform with respect to the volume Λ . We estimate separately in (4.14) the hard-core term (4.12) (lemma 2) and the part involving the interaction potential between the electron and the impurities (lemma 3).

Lemma 2

For $n \ge 2$ and $1 \le k \le n - 1$ one has

$$\int d\mathbf{r}_{k+1} \dots d\mathbf{r}_{n} |S(\mathbf{r}_{1}, \dots, \mathbf{r}_{k} | \mathbf{r}_{k+1} | \dots | \mathbf{r}_{n})| \le \left(\frac{4\pi d^{3}}{3}\right)^{n-k} (n-k-1)! \ k e^{n}$$
 (4.16)

<u>Proof</u>

The sum over connected graphs (4.12) is bounded by a sum on all trees T with vertices k, k+1, ..., n [9]

$$|S(\mathbf{r}_{1},...,\mathbf{r}_{k}|\mathbf{r}_{k+1}|...|\mathbf{r}_{n})| \le \sum_{T} \prod_{(l,m) \in T} (\chi_{q_{l}q_{m}} - 1)$$
 (4.17)

For each tree T the product runs on the n-k bonds of T. Thus one has according to (4.10) $(q_k = \{r_1, ..., r_k\}, q_{k+1} = \{r_{k+1}\}, ..., q_n = \{r_n\})$

$$\int d\mathbf{r}_{k+1} \dots d\mathbf{r}_{n} \prod_{(l, m) \in T} (\chi_{q_{l}q_{m}} - 1) =$$

$$\left[\int d\mathbf{r}_{k+1} \left| \prod_{j=1}^{k} \chi(\mathbf{r}_{j} - \mathbf{r}) - 1 \right| \right]^{d_{k}(T)} \left[\int d\mathbf{r} |\chi(\mathbf{r}) - 1| \right]^{n-k-d_{k}(T)}$$
(4.18)

To obtain (4.18), one integrates over all bonds of the tree T having root q_k with coordination number $d_k(T)$. Using the identity

$$\prod_{j=1}^{k} a_{j} - 1 = \sum_{l=1}^{k} (a_{l} - 1) \prod_{j=l+1}^{k} a_{j}$$
(4.19)

one gets

$$\int d\mathbf{r} \left| \prod_{j=1}^{k} \chi(\mathbf{r}_{j} - \mathbf{r}) - 1 \right| \leq \sum_{l=1}^{k} \int d\mathbf{r} |\chi(\mathbf{r}_{l} - \mathbf{r}) - 1| = k \left(\frac{4\pi}{3} d \right)^{3}$$
 (4.20)

Thus (4.17), (4.18) and (4.20) lead to

$$\int d\mathbf{r}_{k+1} \dots d\mathbf{r}_{n} |S(\mathbf{r}_{1}, \dots, \mathbf{r}_{k} | \mathbf{r}_{k+1} | \dots | \mathbf{r}_{n})| \le \left(\frac{4\pi}{3} d^{3}\right)^{n-k} \sum_{T} k^{d_{k}(T)}$$
(4.21)

One knows [10] that the number of trees T such that $d_k(T) = m$ (m integer, $1 \le m \le n-k$) is $\frac{(n-k-1)!}{(m-1)! (n-k-m)!} (n-k)^{n-k-m}$. Therefore

$$\sum_{T} k^{d_k(T)} = \sum_{m=1}^{n-k} \sum_{T: d_k(T) = m} k^m = (n-k-1)! \sum_{m=1}^{n-k} \frac{k^m}{(m-1)!} \frac{(n-k)^{n-k-m}}{(n-k-m)!}$$

$$\leq (n-k-1)! e^{n-k} \sum_{m=1}^{\infty} \frac{k^m}{(m-1)!} = (n-k-1)! k e^n$$
 (4.22)

Inserting (4.22) into (4.21) gives the result of the lemma.

The application of the lemma 2 to (4.15) leads to the bound

$$\left| h_{nk}^{\Lambda} \right| \leq \left(\frac{4\pi}{3} d^{3} \right)^{n-k} (n-k-1)! k e^{n} \int_{\Lambda} dr_{1} ... dr_{k} \chi_{d}(r_{1},...,r_{k}) J_{k}(r_{1}-x,...,r_{k}-x)$$

$$\leq \left(\frac{4\pi}{3}d^{3}\right)^{n-k}n! e^{n} \int d\mathbf{r}_{1} \dots d\mathbf{r}_{k} \chi_{d}(\mathbf{r}_{1},\dots,\mathbf{r}_{k}) J(\mathbf{r}_{1},\dots,\mathbf{r}_{k})$$
(4.23)

with

$$J_{k}(\mathbf{r}_{1},...,\mathbf{r}_{k}) = \int d\mu_{\beta}(\underline{\omega}) \prod_{j=1}^{k} \left(\exp\left[-V(\mathbf{r}_{j},\underline{\omega})\right] - 1 \right)$$
(4.24)

To obtain (4.23) we have removed the finite volume constraints in the path integral and in the integrals over the impurities (the x dependence drops because $\chi_d(\mathbf{r}_1,...,\mathbf{r}_k)$ is translation invariant). Moreover, we have used (n-k-1)! $k \le n!$ so the inequality holds for $1 \le k \le n$, $n \ge 2$.

Lemma 3

$$\int d\mathbf{r}_{1} \dots d\mathbf{r}_{k} \ \chi_{d}(\mathbf{r}_{1},...,\mathbf{r}_{k}) \ J_{k}(\mathbf{r}_{1},...,\mathbf{r}_{k}) \leq A \frac{e^{\beta B}}{(4\pi\beta)^{3/2}} \left(\beta \ A \ \| \ V \ \|_{1}\right)^{k}$$
(4.25)

where A and B are the constants of lemma 1.

Proof

With (4.3) and $e^{-a} - 1 \le |a|e^{-a}$, $a \le 0$, one has

$$\begin{split} J_{k}(\mathbf{r}_{1},...,\mathbf{r}_{k}) &\leq \int d\mu_{\beta}(\omega) \int_{0}^{\beta} dt_{1}... \int_{0}^{\beta} dt_{k} \prod_{j=1}^{k} |V(\mathbf{r}_{j} - \underline{\omega}(t_{j}))| \cdot \exp\left(-\sum_{j=1}^{k} \int_{0}^{\beta} dt \ V(\mathbf{r}_{j} - \underline{\omega}(t_{j}))\right) \\ &= \sum_{\sigma} \int_{0}^{\beta} dt_{1} \int_{0}^{t_{1}} dt_{2} ... \int_{0}^{t_{k-1}} dk_{k} \int d\mu_{\beta}(\underline{\omega}) \prod_{j=1}^{k} |V(\mathbf{r}_{\sigma(j)} - \underline{\omega}(t_{j}))| \\ \cdot \exp\left(-\sum_{j=1}^{k} \int_{0}^{\beta} dt \ V(\mathbf{r}_{j} - \underline{\omega}(t_{j}))\right) \end{split}$$

$$(4.26)$$

In the second line of (4.26) times are ordered and the sum runs on all permutations of 1, 2, ..., k. The path integral can be performed and expressed in terms of the kernel (3.3). Thus, the bound (4.26) becomes

$$J(\mathbf{r}_{1},...,\mathbf{r}_{k}) \leq \sum_{\sigma} \int_{0}^{\beta} dt_{1} \int_{0}^{t_{1}} dt_{2} ... \int_{0}^{t_{k-1}} dt_{k} \int dy_{1} ... dy_{k} (\mathbf{o} | \exp[-(\beta - t_{1}) H_{\sigma}^{k}] | y_{1}) | V(\mathbf{r}_{\sigma(1)} - y_{1}) |$$

$$.(y_{1} | \exp[-(t_{1} - t_{2}) H_{\sigma}^{k}] | y_{2}) ... | V(\mathbf{r}_{\sigma(k)} - y_{k}) | (y_{k} | \exp[-t_{k} H_{\sigma}^{k}] | \mathbf{o})$$

$$(4.27)$$

where $H_{\sigma}^{(k)} = H^{(k)}(r_{\sigma(1)},...,r_{\sigma(k)})$ is the k-impurities hamiltonian (2.5) with permuted arguments. Thus, using the lemma 1 for $|r_i - r_j| \ge 2d$, one finds

$$\begin{split} J(r_1, ..., r_k) & \leq A^{k+1} \, \mathrm{e}^{\beta B} \sum_{\sigma} \int\limits_{0}^{\beta} \mathrm{d}t_1 \int\limits_{0}^{t_1} \mathrm{d}t_2 \, ... \int\limits_{0}^{t_{k-1}} \mathrm{d}t_k \int \mathrm{d}y_1 \, ... \, \mathrm{d}y_k (\mathsf{o} \, | \, \exp[-2(\beta - t_1) \, H^o] \, | \, y_i) \\ & . \, | \, V(r_{\sigma(1)} - y_1) \, | \, (y_1 \, | \, \exp[-2(t_1 - t_2) H^o] \, | \, y_2) \, ... \, | \, V(r_{\sigma(k)} - y_k) \, | \, (y_k \, | \, \exp[-2t_k \, H^o] \, | \, \mathsf{o}) \, \, (4.28) \end{split}$$

Finally, integrating on the positions of the impurities,

$$\int d\mathbf{r}_{1} \dots d\mathbf{r}_{k} \, \chi_{d} \, (\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) \, J(\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) \leq$$

$$A^{k+1} e^{\beta B} \, \| \, V \, \|_{1}^{k} \sum_{\sigma} \int_{0}^{\beta} dt_{1} \int_{0}^{t_{1}} dt_{2} \dots \int_{0}^{t_{k-1}} dt_{k} \, (\mathbf{o} \, | \exp(-2\beta \, H^{o} \, | \, \mathbf{o}))$$

$$= A \frac{e^{\beta B}}{(4\pi \beta)^{3/2}} \, (\beta A \, \| \, V \, \|_{1})^{k}$$

$$(4.29)$$

IV.3. Proof of proposition 1

We can now prove the first part of the proposition 1. Combining (4.14), (4.23) and (4.29) gives for $n \ge 2$

$$|I_{nk}^{\Lambda}| \le A \frac{e^{\beta B}}{(4\pi\beta)^{3/2}} n! e^{n} \left(\frac{4\pi}{3} d^{3}\right)^{n-k} (\beta A \|V\|_{1})^{k}$$
 (4.30)

and from (4.13)

$$||f_{\Lambda}^{n}(\beta)|| = \sum_{k=1}^{n} \frac{1}{|k!(n-k)!|} ||I_{n|k}^{\Lambda}|| \le \frac{Ae^{\beta B}}{(4\pi\beta)^{3/2}} \left(e^{\left(\frac{4\pi}{3}d^{3} + \beta A \|V\|_{1}\right)} \right)^{n}$$
(4.31)

Thus the series (3.11) converge for $|z| < z_0(\beta)$

$$z_{o}(\beta) = \frac{1}{e} \left(\frac{4\pi}{3} d^{3} + \beta A \| V \|_{1} \right)^{-1}$$
 (4.32)

The existence of the thermodynamic limit (3.12) is also an immediate consequence of the lemma 2 and 3. Since the bound (4.31) is uniform with respect to Λ , it is sufficient by dominated convergence to compute the limit term by term. By the results of the lemma 2 and 3, the integrand in (4.15) is jointly integrable over the product measures $dr_1...dr_n d\mu_{x\beta}(\underline{\omega})$, and therefore, by dominated convergence

$$\lim_{|\Lambda| \to \infty} h_{k}^{\Lambda}(x) = h_{nk}$$

$$= \int d\mathbf{r}_{1} \dots d\mathbf{r}_{n} \chi_{d}(\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) S(\mathbf{r}_{1}, \dots, \mathbf{r}_{k} | \mathbf{r}_{k+1} | \dots | \mathbf{r}_{n}) \int d\mu_{\beta}(\omega) \prod_{j=1}^{k} \left(\exp\left[-V(\mathbf{r}_{j}, \underline{\omega})\right] - 1 \right)$$

$$1 \le k \le n , \quad n \ge 1$$
(4.33)

Hence, writing

$$I_{nk}^{\Lambda} = \frac{1}{|\Lambda|} \int_{\Lambda} dx \left(h_{nk}^{\Lambda}(x) - h_{nk}^{\Lambda}(o) \right) + h_{nk}^{\Lambda}(o)$$
 (4.34)

one obtains

$$\lim_{|\Lambda| \to \infty} I^{\Lambda} = h_{nk} \tag{4.35}$$

provided that the first term in the l.h.s of (4.34) tends to zero as $|\Lambda| \to \infty$. Introducing the characteristic function χ_{Λ} (r) of Λ , this term is majorized by

$$\left| \frac{1}{|\Lambda|} \int_{\Lambda} d\mathbf{x} \left(\mathbf{h}_{n k}^{\Lambda}(\mathbf{x}) - \mathbf{h}_{n k}^{\Lambda}(\mathbf{o}) \right) \right| \leq \int_{\Lambda} d\mathbf{r}_{1} ... d\mathbf{r}_{n} \left[\frac{1}{|\Lambda|} \int_{\Lambda} d\mathbf{x} \left| \prod_{j=1}^{k} \chi_{\Lambda}(\mathbf{r}_{j} + \mathbf{x}) - \prod_{j=1}^{k} \chi_{\Lambda}(\mathbf{r}_{j}) \right| \right] \chi_{d}(\mathbf{r}_{1}, ..., \mathbf{r}_{k}) S(\mathbf{r}_{1}, ..., \mathbf{r}_{k} | \mathbf{r}_{k+1} | ... | \mathbf{r}_{n})$$

$$\cdot \int_{\Lambda} d\mu_{\beta}(\omega) \prod_{j=1}^{k} \left(\exp\left[-V(\mathbf{r}_{j}, \underline{\omega}) \right] - 1 \right)$$

$$(4.36)$$

The bracket in (4.36) is less than 1 and tends to zero as $|\Lambda| \to \infty$ for each fixed configuration of the impurities. Thus (4.36) vanishes as $|\Lambda| \to \infty$, and we conclude that

$$\lim_{|\Lambda| \to \infty} f_{\Lambda}^{n}(\beta) = f^{n}(\beta) = \sum_{k=1}^{n} \frac{1}{k!(n-k)!} h_{nk}$$
(4.37)

with h_{nk} given by (4.33). This completes the proof of proposition 1.

Let us also give the expression of h_{nk} in terms of the original n-impurities hamiltonians (2.5). With the help of the identity

$$\prod_{j=1}^{k} (f_{j}-1) = \sum_{l=1}^{k} \sum_{j_{1} \dots j_{l}}^{k} (-1)^{k-l} (f_{j_{1}} \dots f_{j_{l}}-1)$$
(4.38)

and noting that the integrand of (4.33) is symmetric with respect to the permutations of $r_1,...,r_k$, one obtains

$$h_{nk} = \int d\mathbf{r}_{1} \dots d\mathbf{r}_{n} \ \chi_{d}(\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) S(\mathbf{r}_{1}, \dots, \mathbf{r}_{k} | \mathbf{r}_{k+1} | \dots | \mathbf{r}_{n})$$

$$. \sum_{l=1}^{k} (-1)^{k-l} \frac{k!}{1!(k-l)!} \int d\mu_{\beta}(\omega) \left[\exp[-\beta \sum_{j=1}^{l} V(\mathbf{r}_{j}, \underline{\omega})] - 1 \right]$$
(4.39)

In view of the Feynman-Kac representation of the kernels this is also equal to

$$\begin{split} h_{nk} &= \int d\mathbf{r}_{1} \dots d\mathbf{r}_{n} \ \chi_{d}(\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) \, S(\mathbf{r}_{1}, \dots, \mathbf{r}_{k} | \mathbf{r}_{k+1} | \dots | \mathbf{r}_{n}) \\ & \sum_{l=1}^{k} \ (-1)^{k-l} \ \frac{k!}{l!(k-l)!} \, \left[(\mathbf{o} | \exp[-\beta H^{l}(\mathbf{r}_{1}, \dots, \mathbf{r}_{l})] - \exp[-\beta H^{o}] | \mathbf{o}) \right] \end{split} \tag{4.40}$$

V. The ionisation equilibrium limit

In this section we prove the proposition 2, considering first the case $\lim_{\beta \to \infty} w(\beta) = w < \infty$. As a consequence of proposition 1, one can write

$$(2\pi\beta)^{3/2} f(\beta + \lambda, z(\beta)) = 1 + w(\beta) \exp[-\beta E_0] \operatorname{Tr}(e^{-(\beta + \lambda)H^1} - e^{-(\beta + \lambda)H^0})$$

$$+ (2\pi\beta)^{3/2} \sum_{n=2}^{\infty} (z(\beta))^n f^n(\beta + \lambda)$$
(5.1)

As already explained in (2.25)-(2.28), the term of order one in (5.1) tends to $\operatorname{wexp}(\lambda E_0)$ (the formula (2.27) is justified in appendix D). Thus one gets the result (3.14) if the sum of the terms with $n \ge 2$ vanishes as $\beta \to \infty$. To establish this fact, let us show first that the sum of the terms with large enough $n \pmod{n}$ (say $n \ge N$) goes to zero as $\beta \to \infty$. Indeed, one notes from (3.13) and (4.32) that for any fixed λ and β large

$$z(\beta)/z_{o}(\beta + \lambda) = O(w(\beta) e^{-\beta E_{o}})$$
(5.2)

and since $f^{n}(\beta + \lambda)$ satisfies the bound (4.31) (with β replaced by $\beta + \lambda$), one has

$$(2\pi\beta)^{3/2} \sum_{n=N}^{\infty} (z(\beta))^n f^n(\beta + \lambda) \le A \left(\frac{\beta}{2(\beta + \lambda)}\right)^{3/2} e^{(\beta + \lambda)B} \left(\frac{z(\beta)}{z_o(\beta + \lambda)}\right)^N \left(1 - \frac{z(\beta)}{z_o(\beta + \lambda)}\right)$$

$$= O\left((w(\beta))^N \exp[-\beta(NE_o - B)]\right)$$
(5.3)

This tends to zero for $N > B/E_0$.

It remains to show that each of the terms with $2 \le n \le B/E_0$ also vanishes as $\beta \to \infty$. In the following, C will always denote a generic constant independent of β ($\beta > 1$) and of the location of the impurities. According to (4.37), we estimate the quantities h_{nk} defined by (4.33). At this point, one needs to bound the h_{nk} in terms of the groundstate energies of the n-impurities hamiltonian H^n ($n \ge 2$) and to use the stability condition (2.7). For this we make the following decomposition. For a fixed configuration of impurities $r_1,...,r_k$, let $B(r_i, a)$ denote the ball of radius a

centerd at \mathbf{r}_{j} . To each partition $P = \{P', P''\}$ of $\{1,...,k\}$ in two subsets P', P'' one associates the set \mathcal{D}_{P} consisting of Browninan paths intersecting only the balls $B(\mathbf{r}_{j'}, \mathbf{a}), j \in P'$, i.e.

$$\mathcal{D}_{P} = \left\{ (\underline{\omega}(t) \mid \inf_{t} |\underline{\omega}(t) - r_{j}| \le a, j \in P', \text{ and } \inf_{t} |\underline{\omega}(t) - r_{j}| > a, j \in P'') \right\}$$
 (5.4)

Clearly, the space of all Brownian paths is the disjoint union of the \mathcal{D}_P where P runs over all such partitions. It is therefore sufficient to study h_{nk}^P given by the same expression than (4.33) with the functional integral restricted to \mathcal{D}_P . Using the lemma 2, one has

$$|h_{nk}^{P}| \le C \int d\mathbf{r}_{1} \dots d\mathbf{r}_{k} \chi_{d}(\mathbf{r}_{1}, \dots, \mathbf{r}_{k}) \int_{\mathcal{D}_{P}} d\mu_{\beta}(\underline{\omega}) \prod_{j=1}^{k} \left(\exp[-V(\mathbf{r}_{j}, \underline{\omega})] - 1 \right)$$
(5.5)

Choosing $a \ge R$ (R is the constant occurring in the condition (2.3)), we remark that for $j \in P$ "

$$V(\mathbf{r}_{j'}\underline{\omega}) = \int_{0}^{\beta} dt \ V(\mathbf{r}_{j} - \underline{\omega}(t)) \ge -\frac{M}{a^{\eta}}$$
 (5.6)

and

$$\exp[-V(\mathbf{r}_{\mathbf{j'}}\underline{\omega})] - 1 \le |V(\mathbf{r}_{\mathbf{j'}}\underline{\omega})| \exp\left(\beta \frac{M}{a^{\eta}}\right)$$
 (5.7)

Hence

$$\begin{split} &\mid h_{nk}^{\;P} \mid \leq C \; exp \left((k-l) \; \beta \frac{M}{a^{\eta}} \right). \\ &\cdot \int dr_1 \ldots dr_k \; \chi_d(r_1, ..., r_k) \int\limits_{\mathcal{D}_P} d\mu_{\beta}(\!\omega\!) \prod_{j \in P''} |V(r_j, \!\omega\!)| \prod_{j \in P'} \left(exp[-V(r_j, \!\omega\!)] - 1 \right) \; (5.8) \end{split}$$

In (5.8), by a relabelling of the $r_{j'}$ the partition P is of the form P'= (1,2,...,l), P" = (l + 1, ..., k) with some l, $0 \le l \le k$. If l = 0 (resp. k), P' (resp. P") is empty. The r.h.s. of (5.8) increases if one relaxes the hard core condition for the impurities $r_{j'}$ j = l + 1, ..., k and the exclusion of the paths from the balls $B(r_{j'}, a)$, j = l + 1, ..., k in

(5.4). One can then integrate
$$\prod_{j=l+1}^{k} |V(\mathbf{r}_{j}, \underline{\omega})|$$
 and get

$$\begin{split} &|h_{nk}^{P}| \leq C \left(\beta \|V\|_{1}\right)^{k-l} \exp\left((k-l) \beta \frac{M}{a^{\eta}}\right) \\ &|\int d\mathbf{r}_{1} \dots d\mathbf{r}_{l} \chi_{d}(\mathbf{r}_{1}, ..., \mathbf{r}_{l}) \int d\mu_{\beta}(\underline{\omega}) \chi_{a}(\underline{\omega}; \mathbf{r}_{1}, ..., \mathbf{r}_{l}) \prod_{j=1}^{l} \left(\exp[-V(\mathbf{r}_{j}, \underline{\omega})] - 1\right), l \geq 1 \\ &|h_{nk}^{P}| \leq \frac{C}{(2\pi\beta)^{3/2}} \left(\beta \|V\|_{1}\right)^{k} \exp\left(k\beta \frac{M}{a^{\eta}}\right) , l = 0 \end{split} \tag{5.9.b}$$

The application of the identity (4.38) to (5.9.a) gives

$$|h_{nk}^{P}| \le C \left(\beta \|V\|_{1}\right)^{k-l} \exp\left((k-l) \beta \frac{M}{a^{\eta}}\right) \sum_{m=1}^{l} (-1)^{l-m} \frac{l!}{(l-m)! \ m!} \ u_{lm} \quad (5.10)$$

with $1 \le l \le k$

$$\begin{aligned} \mathbf{u}_{lm} = & \int d\mathbf{r}_{1} \, ... \, d\mathbf{r}_{l} \, \chi_{d} \, (\mathbf{r}_{1'} \, ..., \, \mathbf{r}_{l}) \int d\mu_{\beta}(\underline{\omega}) \, \chi_{a} \, (\underline{\omega}; \, \mathbf{r}_{1'} \, ..., \, \mathbf{r}_{l}) \\ & \cdot \left(\exp[-V^{m}(\mathbf{r}_{1'} \, ..., \, \mathbf{r}_{m'} \, \underline{\omega})] - 1 \right) \end{aligned} \tag{5.11}$$

$$V^{m}(\mathbf{r}_{1'} \, ..., \, \mathbf{r}_{m'} \, \underline{\omega}) = \sum_{i=1}^{m} \, V(\mathbf{r}_{j'} \, \underline{\omega})$$

In (5.9.a) and (5.11) $\chi_a(\underline{\omega}; r_1, ..., r_l)$ is the characteric function of the set

$$\mathcal{D}\mathbf{r}_{1}, ..., \mathbf{r}_{1} = \left\{ \begin{array}{cc} \underline{\omega}(t) & \underline{\omega}(0) = 0 \text{ and } \inf_{t} |\underline{\omega}(t) - \mathbf{r}_{j}| \leq a, j = 1, ..., 1 \end{array} \right\}$$
 (5.12)

Thus the estimation of h_{nk}^P for $l \ge 1$ is reduced to that of the u_{lm} . For this, one needs the following lemmas. The lemma 4 estimates the probability of the set (5.12) for $l \ge 2$.

Lemma 4

Let a be a fixed positive number, then for $1 \ge 2$

$$\chi_{a} (\underline{\omega}; \mathbf{r}_{1}, ..., \mathbf{r}_{l}) \leq \prod_{j=2}^{l} \widetilde{\chi}_{a} (\underline{\omega}; \mathbf{r}_{j} - \mathbf{r}_{1})$$
 (5.13)

with $\widetilde{\chi}_a^{}\left(\underline{\omega}; r\right)$ the characteristic function of the set

$$\left\{\begin{array}{cc} \underline{\omega}(s) \mid \underline{\omega}(0) = 0 \text{ and } \sup_{s} \mid \underline{\omega}(s) \ge \frac{1}{2} \mid r \mid -a \end{array}\right\}$$
 (5.14)

Furthermore there exists constants C_a and D independent of β ($\beta > 1$) such that

$$\int d\mu_{\beta}(\omega) \prod_{j=2}^{l} \widetilde{\chi}_{a}(\omega; r_{j} - r_{1}) \le C_{a} \prod_{j=2}^{l} \exp\left(-D \frac{|r_{j} - r_{1}|^{2}}{\beta}\right), 1 \ge 2$$
(5.15)

The lemma 5 gives us the suitable connection with the groundstate energy of the n-impurities hamiltonian $H^n = H^0 + V^n$.

Lemma 5

Let ϵ be a fixed positive number, $0<\epsilon<\beta$. There exists a constant C_{ϵ} (independent of β and $r_1,...,r_{n'}$ | r_i - r_i | \geq 2d) such that

$$\operatorname{Tr} |V^{n}| \exp[-\beta H^{n}] \leq C_{\varepsilon} ||V||_{1} \exp[-(\beta - \varepsilon) \operatorname{Inf} \operatorname{spec} (H^{0} + V^{n})]$$
 (5.16)

The lemmas are proven in the appendices C and D. We now come back to the estimation of u_{lm} . We use again the inequality $e^{-y} - 1 \le |y| e^{-y}$ ($y \le 0$) and then, for fixed r_1 , change the integration variables r_2 , ..., r_l to $r_2 + r_1$, ..., $r_l + r_1$:

$$\begin{aligned} u_{lm} &\leq \int d\mathbf{r}_{2} \dots d\mathbf{r}_{l} \, \chi_{d} \, (\mathbf{o}, \, \mathbf{r}_{2}, \, ..., \, \mathbf{r}_{l}) \, \int d\mathbf{r}_{1} \int d\mu_{\beta}(\underline{\omega}) \, \left| V^{n}(\mathbf{r}_{1}, \, \mathbf{r}_{2} + \mathbf{r}_{1}, \, ..., \, \mathbf{r}_{m} + \mathbf{r}_{1}, \, \underline{\omega}) \right| \\ \chi_{a} \, (\underline{\omega}; \, \mathbf{r}_{1}, \, \mathbf{r}_{2} + \mathbf{r}_{1}, \, ..., \, \mathbf{r}_{l} + \mathbf{r}_{1}) \, \exp \left(- \, V^{m}(\mathbf{r}_{1}, \, \mathbf{r}_{2} + \mathbf{r}_{1}, \, ..., \, \mathbf{r}_{l} + \mathbf{r}_{1}, \, \underline{\omega}) \right) \end{aligned} \tag{5.17}$$

The application of the Hölder inequality to the product measures $dr_1 d\mu_{\beta}(\underline{\omega})$ including the weight factor $|V^n(r_1, r_2 + r_1, ..., r_m + r_1, \underline{\omega})|$ gives

$$\begin{split} u_{lm} & \leq \int d\mathbf{r}_{2} \dots d\mathbf{r}_{l} \chi_{d}(\mathbf{o}, \mathbf{r}_{2}, ..., \mathbf{r}_{l}) \, . \\ & \left[\int d\mathbf{r}_{1} \int d\mu_{\beta}(\underline{\omega}) \, \left| V^{m}(\mathbf{r}_{1}, \mathbf{r}_{2} + \mathbf{r}_{1}, ..., \mathbf{r}_{m} + \mathbf{r}_{1}, \underline{\omega}) \right| \, \chi_{a}(\underline{\omega}; \, \mathbf{r}_{1}, \, \mathbf{r}_{2} + \, \mathbf{r}_{1}, \, ..., \, \mathbf{r}_{l} + \, \mathbf{r}_{1}) \, \right]^{1/p} \\ & \left[\int d\mathbf{r}_{1} \int d\mu_{\beta}(\underline{\omega}) \, \left| V^{m}(\mathbf{r}_{1}, \mathbf{r}_{2} + \mathbf{r}_{1}, ..., \mathbf{r}_{m} + \mathbf{r}_{1}, \underline{\omega}) \right| \right. \\ & \left. \exp \left(-q \, V^{m}(\mathbf{r}_{1}, \mathbf{r}_{2} + \mathbf{r}_{1}, ..., \mathbf{r}_{m} + \mathbf{r}_{1}, \underline{\omega}) \right) \right]^{1/q} \end{split} \tag{5.18}$$

with $\frac{1}{p} + \frac{1}{q} = 1$. One remarks that the second bracket is equal to

$$\beta Tr \left| V^{m}(\mathbf{o}, \mathbf{r}_{2}, ..., \mathbf{r}_{m}) \right| \exp \left[-\beta (H^{o} + q V^{m}(\mathbf{o}, \mathbf{r}_{2}, ..., \mathbf{r}_{m})) \right]$$
 (5.19)

and thus, by the lemma 5, it is bounded by

(5.22)

$$C \beta \|V\|_{1} \exp \left[(\beta - \varepsilon) E^{m}(q) \right]$$
(5.20)

with

$$E^{m}(q) = -\inf_{\mathbf{r}_{2} \dots \mathbf{r}_{m}} \inf \operatorname{spect} \left(H^{o} + q V^{m}(\mathbf{o}, \mathbf{r}_{2}, ..., \mathbf{r}_{m}) \right)$$
 (5.21)

Thus (5.18) - (5.21) lead to

$$\begin{split} \mathbf{u}_{lm} & \leq \left(C \; \beta \; \| \; V \; \|_{1} \right)^{1/q} \exp \left[\left(\beta - \epsilon \right) \frac{1}{q} E^{m}(q) \right] \int d\mathbf{r}_{2} \; ... \; d\mathbf{r}_{l} \; \chi_{d}(\mathbf{o}, \, \mathbf{r}_{2}, \, ..., \, \mathbf{r}_{l}). \\ & \left[\; \int d\mathbf{r}_{1} \int d\mu_{\beta}(\underline{\omega}) \; \left| V^{m}(\mathbf{r}_{1}, \, \mathbf{r}_{2} + \mathbf{r}_{1}, ..., \, \mathbf{r}_{m} + \mathbf{r}_{1}, \, \underline{\omega}) \right| \; \; \chi_{a}(\underline{\omega}; \, \mathbf{r}_{1}, \, \mathbf{r}_{2} + \mathbf{r}_{1}, \, ..., \, \mathbf{r}_{l} + \mathbf{r}_{l}) \; \right]^{1/p} \end{split}$$

When $l \ge 2$, thanks to (5.13), the integrand in the bracket has a bound independent of r_1 except for the potential part, whose r_1 -integral is bounded by

$$\int d\mathbf{r}_{1} \left| V^{m}(\mathbf{r}_{1}, \mathbf{r}_{2} + \mathbf{r}_{1}, ..., \mathbf{r}_{m} + \mathbf{r}_{1}, \underline{\omega}) \right| \leq m \beta \|V\|_{1}$$
(5.23)

Droping the hard core constraint and taking (5.13), (5.15) and (5.23) into account together with $\int dr \exp\left(-\frac{Dr^2}{\beta}\right) = C \beta^{3/2}$ gives the result

$$\mathbf{u}_{lm} \leq \mathbf{C}_{\mathbf{a}, \boldsymbol{\epsilon}, \mathbf{q}} \left(\boldsymbol{\beta} \parallel \mathbf{V} \parallel_{1} \right) \left(\boldsymbol{\beta}^{3/2} \right)^{l-1} \exp \left[\boldsymbol{\beta} \frac{1}{\mathbf{q}} \mathbf{E}^{\mathbf{m}} (\mathbf{q}) \right]$$
 (5.24)

When l = 1, one can use χ_a ($\underline{\omega}$; \mathbf{r}_1) ≤ 1 instead of (5.13) and it follows that (5.24) holds also in this case. Each term of the sum (5.10) has a bound of the form

$$C \beta^{k+(l-1)/2} \exp\left((k-l) \beta \frac{M}{a^{\eta}}\right) \exp\left[\beta \frac{1}{q} E^{m}(q)\right], \qquad (5.25)$$

Since the binding energies are convex functions of the coupling parameter, $E^m(q)$ (a supremum of convex functions) is still convex. Moreover, we know that for q in a neighbourhood of 1, it is bounded above (see the remark at the end of Section III). Thus, the function $E^m(q)$ is continuous at q = 1. Hence, for any $\delta > 0$, one can find q sufficiently close to one (q > 1) such that for all $m, 1 \le m \le n$

$$\frac{1}{q}E^{m}(q) \leq E^{m}(1) + \delta \tag{5.26}$$

and by the stability bound (2.7)

$$\frac{1}{q}E^{m}(q) \leq mK + \delta \qquad , m \geq 2$$

$$\frac{1}{q}E^{1}(q) \leq m_{o} + \delta \qquad , m = 1$$
 (5.27)

Moreover, choosing a such that $\frac{M}{a} \le K' < K$, one has

$$(k-1) \frac{M}{a^{\eta}} \le (k-1) K' \le (n-m) K'$$
 (5.28)

With (5.27) and (5.28), we conclude that for all m, l, k with $1 \le m \le l \le k \le n$ ($n \ge 2$) and all $\beta \ge 1$, the quantity (5.25) is majorized by

$$C \left(\beta^{3/2}\right)^{n} \exp \left[\beta \left(nK + \delta\right)\right] , m \ge 2$$

$$C \left(\beta^{3/2}\right)^{n} \exp \left[\beta \left((n-1)K' + E_{o} + \delta\right)\right] , m = 1$$
(5.29)

Comparing with (5.9b), one notes that (5.29) is also an upper bound of h_{nk}^{P} for l = 0. Since $f^{n}(\beta)$ has been decomposed into a finite number of terms (the sums (4.37), (5.10) and the sum over partitions), $f^{n}(\beta)$ satisfies the estimate

$$f^{n}(\beta) \le C_{1} (\beta^{3/2})^{n} \exp \left[\beta(n K + \delta)\right] + C_{2} (\beta^{3/2})^{n} \exp \left[\beta(n-1) K' + E_{0} + \delta\right]$$
 (5.30)

where C_1 and C_2 are appropriate constants depending on n, a, ϵ , q but not on β (β > 1). Thus one gets

$$(2\pi\beta)^{3/2} \left(z(\beta) \right)^n f^n(\beta + \lambda) = O\left(\beta^{3/2} \left(w(\beta) \right)^n \exp\left[-\beta \left(n(E_o - K) - \delta \right) \right] \right)$$

$$+ O\left(\beta^{3/2} \left(w(\beta)^n \right) \exp\left[-\beta \left(((n-1)(E_o - K) - \delta) \right) \right] \right), \quad n \ge 2$$

$$(5.31)$$

Since $K' < K < E_o$ and $\lim_{\beta \to \infty} w(\beta) = w < \infty$, (5.31) vanishes as $\beta \to \infty$ provided that δ is small enough. This conclude the proof of (3.14). Since the convergence of the Laplace transforms implies the convergence of the corresponding measures [10], $P(.; \beta, z(\beta))$ tends to $\frac{1}{1+w} \delta_o(.) + \frac{w}{1+w} \delta_{-E_o}(.)$, and thus (3.15) follows.

If $w(\beta)$ diverges as $\beta \to \infty$, the first order term in (5.1) also diverges like $w(\beta)$. Moreover, if $w(\beta) = O(\exp(\beta(E_o - K)))$, it is the most diverging term of the series. Indeed, for $n \ge 2$, one finds in this case from (5.31)

$$\frac{(2\pi\beta)^{3/2} \left(z(\beta)\right)^{n} f^{n} (\beta+\lambda)}{w(\beta)} = O\left(\beta^{3/2} \exp\left(-\beta(E_{o} - K - \delta)\right)\right)$$

$$+ O\left(\beta^{3/2} \exp\left(-\beta\left((n-1)(K - K') - \delta\right)\right)\right)$$
(5.32)

which tends to zero when δ is sufficiently small. One sees on (5.3) that the same is true for the sum of the terms $n \ge N$, N large enough. This means that

$$(2\pi\beta)^{3/2} f(\beta + \lambda z(\beta)) = w(\beta) e^{\lambda E_0} + o(w(\beta))$$
(5.33)

and

$$\lim_{\beta \to \infty} \frac{f(\beta + \lambda, z(\beta))}{f(\beta, z(\beta))} = e^{\lambda E_0}$$
 (5.34)

and so $\gamma_i = 0$.

VI. Spectral properties

In this section we show for any potential satisfying (2.1)-(2.3) that the stability condition (2.7) can be fullfilled with a suitable choice of the hard core radius. More precisely, one has the following proposition

Proposition 3

For any potential V satisfying (2.1)-(2.3) and impurity with hard core diameter d, there exists a constant E(V, d) independent of n and \mathbf{r}_1 , ..., \mathbf{r}_n $n \ge 2$, such that

inf spec
$$H^n(r_1, ..., r_n) \ge -E(V, d)$$
, $n \ge 2$

Moreover

$$\lim_{d \to \infty} E(V, d) = E_0 \tag{6.1}$$

As a consequence of (6.1), one can choose $d = d_0$ large enough so that

$$E(V, d_o) < 2 E_o \tag{6.2}$$

Hence (2.7) holds with $K = \frac{E(V, d_0)}{2}$. We discuss at the end of the section the order of magnitude of d_0 for some special potentials (square well, Yukawa).

Proof of proposition 3

The quadratic form associated to H^n (r_1 , ..., r_n) has the same domain as that of $H^0 = -\frac{1}{2} \Delta$ i.e. the Sobolev spaces \mathcal{H}^1 (\mathbb{R}^3) where

$$\mathcal{H}^{1} = \{ \psi(\mathbf{x}) \mid \psi \in \mathcal{L}^{2}(\mathbb{R}^{3}) \text{ and } \underline{\nabla} \psi(\mathbf{x}) \in \mathcal{L}^{2}(\mathbb{R}^{3}) \}$$
 (6.3)

and one has

$$\inf \operatorname{spect} H^{n} = \inf_{\psi \in \mathcal{H}^{1}} Q^{n}(\psi) \tag{6.4}$$

with

$$Q^{n}(\psi) = \frac{1}{2} \int dx | \nabla \psi(x) |^{2} + \int dx V^{n}(x) | \psi(x) |^{2}$$
(6.5)

Let $B_j = B(r_j, d)$ be the ball of center r_j and radius d, with characteristic function $\chi_j(x)$ $(\tilde{\chi}_j(x))$ is the characteristic function of $\mathbb{R}^3 \setminus B_j$. For $|r_i - r_j| \ge 2d$, the balls do not overlap, and dropping part of the kinetic energy, one has

$$Q^{n}(\psi) \geq \sum_{j=1}^{n} \left[\frac{1}{2} \int dx \, \chi_{j}(x) \, | \, \underline{\nabla} \, \psi(x) \, |^{2} + \int dx \, \chi_{j}(x) \, V(x - r_{j}) \, | \, \psi(x) \, |^{2} \right]$$

$$+ \int dx \, \sum_{j} \widetilde{\chi}_{j}(x) \, V(x - r_{j}) \, | \, \psi(x) \, |^{2}$$

$$(6.6)$$

We first give a lower bound for the last term of (6.6). Recalling $V(x) \ge -\frac{M}{|x|\eta}$ for $|x| \ge R$ (see (2.3)), we get for any fixed x

$$\sum_{j}^{n} \widetilde{\chi}_{j}(x) V(x - \mathbf{r}_{j}) = \sum_{|\mathbf{x} - \mathbf{r}_{j}| \leq R} \widetilde{\chi}_{j}(x) V(x - \mathbf{r}_{j}) + \sum_{|\mathbf{x} - \mathbf{r}_{j}| > R} \widetilde{\chi}_{j}(x) V(x - \mathbf{r}_{j})$$

$$\geq - \sup_{|\mathbf{x}| \geq d} |V(\mathbf{x})| \left(\frac{R}{d}\right)^{3} - K_{o}$$

$$(6.7)$$

In (6.7), $\sup_{|\mathbf{x}| \ge d} |V(\mathbf{x})|$ is finite since $V(\mathbf{x})$ is bounded except possibly at the origin $|\mathbf{x}| \ge d$ (condition (2.2)). The summation on the \mathbf{r}_j with $|\mathbf{x} - \mathbf{r}_j| > R$ has been estimated as in (3.33)-(3.34) and K_o is the constant (3.35) with t = 0. Hence

$$\int dx \sum_{j}^{n} \widetilde{\chi}_{j}(x) V(x-r_{j}) |\psi(x)|^{2} \ge -\left[\sup_{|x| \ge d} |V(x)| \left(\frac{R}{d}\right)^{3} + K_{o} \right] \int dx |\psi(x)|^{2}$$
 (6.8)

To estimate the first term in the r.h.s. of the inequality (6.6), it is useful to introduce the forms

$$Q_{\Lambda, m}(\psi) = \frac{1}{2m} \int_{\Lambda} dx |\underline{\nabla}(x)|^2 + \int_{\Lambda} dx |\psi(x)|^2$$
(6.9)

where Λ c \mathbb{R}^3 , m > 0 and $\psi \in \mathcal{H}^1$. Let $\theta_{\epsilon}(x)$ be a C_0^{∞} function with support in $B = B(\mathbf{o}, d)$ such that $0 \le \theta_{\epsilon}(x) \le 1$, $\theta_{\epsilon}(x) = 1$ for $|x| \le d$ $(1 - \epsilon)$ and $|\nabla \theta_{\epsilon}(x)| \le 1/\epsilon d$, $0 < \epsilon < 1$. We note that

$$Q_{B, m}(\theta_{\varepsilon}\psi) = \frac{1}{2m} \int dx \, |\underline{\nabla}(\theta_{\varepsilon}(x)\psi(x))|^2 + \int dx \, |\nabla(x)| \, |\theta_{\varepsilon}(x)\psi(x)|^2 \qquad (6.10)$$

The r.h.s. of (6.10) is the quadratic form associated with the one-impurity hamiltonian $\frac{1}{2m}H_o + V$ with ground state energy $-E_o(m)$ ($E_o(m) > 0$). Since $\theta_\epsilon \psi \in \mathcal{H}^1$, $Q_{B,m}$ ($\theta_\epsilon \psi$) is bounded below by

$$Q_{B, m}(\theta_{\varepsilon}\psi) \ge -E_{o}(m) \int dx |\theta_{\varepsilon}(x)\psi(x)|^{2} \ge -E_{o}(m) \int_{B} dx |\psi(x)|^{2}$$
(6.11)

One obtains a majoration of $Q_{B, m}(\theta_{\epsilon}\psi)$ in terms of $Q_{B, 1}(\psi)$ in the following way. Using the Schwartz inequality and the properties of $\theta_{\epsilon}(x)$, one has

$$\int dx \, |\underline{\nabla} \left(\theta_{\varepsilon}(x) \psi(x) \right)|^{2} \leq \int dx \, \theta_{\varepsilon}^{2}(x) \, |\underline{\nabla} \psi(x)|^{2} + \int dx \, |\underline{\nabla} \theta_{\varepsilon}(x)|^{2} \, |\psi(x)|^{2}$$

$$+ 2 \int dx \, \theta_{\varepsilon}(x) \, |\psi(x)| \, |\underline{\nabla} \theta_{\varepsilon}(x)| \, |\underline{\nabla} \psi(x)|^{2}$$

$$\leq \int dx \, \theta_{\varepsilon}^{2}(x) \, |\underline{\nabla} \psi(x)|^{2} + \int dx \, |\underline{\nabla} \psi(x)|^{2} \, |\psi(x)|^{2}$$

$$+ 2 \left(\int dx \, \theta_{\varepsilon}^{2}(x) \, |\psi(x)|^{2} \right)^{1/2} \left(\int dx \, |\underline{\nabla} \theta_{\varepsilon}(x)|^{2} \, |\underline{\nabla} \psi(x)|^{2} \right)^{1/2}$$

$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int dx \, |\psi(x)|^{2} + \frac{2}{(\varepsilon d)^{2}} \left(\int_{B} dx \, |\psi(x)|^{2} \right)^{1/2} \left(\int_{B} dx \, |\underline{\nabla} \psi(x)|^{2} \right)^{1/2}$$

$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int_{B} dx \, |\psi(x)|^{2} + \frac{2}{(\varepsilon d)^{2}} \left(\int_{B} dx \, |\psi(x)|^{2} \right)^{1/2} \left(\int_{B} dx \, |\underline{\nabla} \psi(x)|^{2} \right)^{1/2}$$

$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int_{B} dx \, |\psi(x)|^{2} + \frac{2}{(\varepsilon d)^{2}} \left(\int_{B} dx \, |\psi(x)|^{2} \right)^{1/2}$$

$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int_{B} dx \, |\psi(x)|^{2}$$

$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int_{B} dx \, |\psi(x)|^{2}$$

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$$\leq \int dx \, |\underline{\nabla} \psi(x)|^{2} + \frac{1}{(\varepsilon d)^{2}} \int_{B} dx \, |\psi(x)|^{2}$$

where the last inequality holds for any m > 1. Furthermore, noting that $V(x)(\theta_s^2(x) - 1) \ge 0$, we have

$$\int_{B} dx \ V(x) \left(\theta_{\varepsilon}^{2}(x) - 1\right) |\psi(x)|^{2} \leq \widetilde{V}_{d} \int_{B} dx |\psi(x)|^{2}$$

$$\widetilde{V}_{d} = \sup_{|x| \geq d(1-\varepsilon)} |V(x)|$$
(6.13)

implying

$$\int dx \ V(x) \ \theta_{\varepsilon}^{2}(x) \ |\psi(x)|^{2} \le \int_{B} dx \ V(x) \ |\psi(x)|^{2} + \widetilde{V}_{d} \int_{B} dx \ |\psi(x)|^{2}$$
 (6.14)

The combination of (6.12) and (6.14) leads to

$$Q_{B, m}(\theta_{\varepsilon} \psi) \le \left(Q_{B; 1}(\psi) + \frac{1}{2(\varepsilon d)^{2}(m-1)} + \widetilde{V}_{d}\right) \int_{B} dx |\psi(x)|^{2}, m > 1$$
 (6.15)

Finally, taking (6.11) into account

$$Q_{B,1}(\psi) \ge -\left(E_{0}(m) + \frac{1}{2(\varepsilon d)^{2}(m-1)} + \tilde{V}_{d}\right) \int_{B} dx |\psi(x)|^{2}$$
(6.16)

One notes that the brackets in the sum (6.6) are equal to $Q_{B,1}(\psi_j)$ where $\psi_i(x) = \psi(x - r_i)$. Therefore, a lower bound for $Q^n(\psi)$ is provided by (6.16) and (6.8):

$$Q^{n}(\psi) \ge -\left(E_{0}(m) + \frac{1}{2(\varepsilon d)^{2}(m-1)} + \widetilde{V}_{d}\left(\left(\frac{R}{d}\right)^{3} + 1\right) + K_{0}\right) \int dx |\psi(x)|^{2}$$
 (6.17)

 $0 < \varepsilon < 1$, m > 1.

For a fixed ε , the lower bound E(V, d) of proposition 3 can be chosen as the constant of (6.17) evaluated at m = 1 + $^{1}/_{d}$. Clearly \tilde{V}_{d} and \tilde{K}_{o} are $O(^{1}/_{d\eta})$ (as can be checked from (3.35)), and $\tilde{E}_{o}(1 + ^{1}/_{d})$ tends to $\tilde{E}_{o}(1) = \tilde{E}_{o}$ as $d \to \infty$. This establishes (6.1) and concludes the proof of proposition 3.

We discuss possible choices of the hard core radius d_0 in order to fulfil the condition (6.2).

(i) Square well

For a bounded potential (with $V_0 = -\inf_X V(x) > 0$), we can first let $m \to \infty$ and then $\varepsilon \to o$ in (6.17). In this limit, $E_0(m)$ tends to V_0 and $V_d = \sup_{\|x\| \ge d} \|V(x)\|$, so the constant in (6.17) is explicitly expressed in term of the potential. Furthermore,

if V(x) has compact support with radius a, it is clear that the constant reduces to V_0 , and the condition (6.2) to

$$V_0 < 2 E_0$$
 (6.18)

provided that $d_o \ge a$. For example, a square well potential of depth $-V_o$ and radius a satisfies (6.18) when $\frac{1}{2}a^2V_o > 1$.

(ii) Yukawa potential

We consider the screened Coulomb potential between two charges (e, -e), $V(x) = -e^2 \frac{1}{r} \exp{(-r/a)}$, r = |x|, with screening length a (obviously V(x) satisfies the hypothesis (2.1)-(2.3)). Measuring all lengths in units of $a_B = \frac{1}{e^2} (a_B$ is the Bohr radius of an hydrogen atom of mass one), and energies in units of a_B^{-2} , the one impurity hamiltonian with mass m reads

$$H = -\frac{1}{2m}\Delta - \frac{\exp(-r/a)}{r}$$
 (6.19)

We make the choices $\varepsilon = 1/2$ and R = d in (6.17). Setting $\alpha = d/a$, the last two terms of the constant in (6.17) give the contribution

$$F(\alpha) = 2 \sup_{|\mathbf{x}| \ge d/2} |V(\mathbf{x})| + K_0 = 2 V\left(\frac{d}{2}\right) + \sum_{k=1}^{\infty} ((k+1)^3 - k^3) V(kd)$$

$$= \frac{1}{a} \left[2 \frac{e^{-\alpha/2}}{\alpha} + \sum_{k=1}^{\infty} (3k^2 + 3k + 1) \frac{e^{-k\alpha}}{k\alpha} \right]$$

$$= \frac{1}{\alpha a} \left[2 e^{-\alpha/2} + 6 \frac{e^{-\alpha}}{1 - e^{-\alpha}} + |\ln(1 - e^{-\alpha})| \right]$$
(6.20)

In the expression (3.35) of K_0 we have used the value of the potential itself instead of the weak bound (2.3). Then, the inequality (6.2) becomes

$$E_0(m) + \frac{2}{(\alpha a)^2 (m-1)} + F(\alpha) < 2E_0 = 2E_0(1)$$
 (6.21)

The numerical values of the ground state energies $E_o(m)$ of the hamiltonian (6.19) can be found for several values of m in the table I of ref. [11]. When $a \ge 3$, we have checked that it is possible to satisfy the inequality (6.21)with $\alpha = 2$ (with suitable values of m > 1). If a is large enough ($a \ge 30$), one can even take $\alpha = 1$. Thus, in this case, (6.2) can certainly be satisfied with the choice $d_0 = 2a$.

In these two examples, at least, one sees that the stability condition (2.7) will hold when the hard core radius has about the same size as the range of the attractive potential (i.e. $d \approx a$).

To conclude this section, we estimate the order of magnitude of the constant B in (3.16) for the one impurity hamiltonian (6.19) with m = 1. For this, one notes that

$$\int dy \, Q_{t}(x-y) \, | \, V(y) \, | = \int_{0}^{t} ds \int dy \, \frac{\exp\left(\frac{-|x-y|^{2}}{2s}\right)}{(2\pi s)^{3/2}} \, \frac{\exp\left(\frac{-|y|}{a}\right)}{|y|}$$

$$= \frac{1}{2\pi^{2}} \int_{0}^{t} ds \int dk \, e^{-ikx} \, e^{-k^{2} s/2} \, \frac{1}{k^{2} + a^{-2}} , \quad k = |k| \quad (6.22)$$

takes its maximum at x = 0. Hence, one finds from (3.17).

$$v(t) = \sqrt{\frac{2}{\pi}} \int_{0}^{t} ds \frac{1}{s^{3/2}} \int_{0}^{\infty} dy \, y \, \exp\left(-\frac{y^{2}}{2s} - \frac{y}{a}\right) , y = |y|$$

$$= \frac{4}{\sqrt{2\pi}} t^{1/2} + \frac{t}{a^{3}} + O(t^{3/2})$$
(6.23)

From the proof of the lemma 1 (see (3.20) and (3.24)), one has

$$B = \frac{D}{2} = \frac{1}{4 t_0} \ln \frac{1}{1 - 4v(t)}$$
 $v(t) < 1/4$ (6.24)

For a \geq 3, the smallest value of B obtained from (6.23) and (6.24) is roughly B \approx 25 with t_o \approx 0,012. On the other hand, the ground state energy E_o of (6.19) (with m = 1) ranges from 0,23 to 0,5 when a \geq 3. So in general B is much larger than E_o, and this will also be the case for the n-impurities hamiltonians.

VII. Comments and conclusions

Information can also be obtained on the momentum and positional distribution of the electron in the ionization equilibrium limit. The techniques are the same as in the preceding sections and we only sketch the arguments.

We consider first the Fourier transform

$$\langle e^{i\underline{\lambda}} \cdot P \rangle = \int e^{i\underline{\lambda}} \cdot k \ p(dk; z, \beta)$$
 (7.1)

of the probability measure giving momentum distribution of the electron. In the finite volume system, $\langle e^{i\underline{\lambda}} \cdot P \rangle_{\Lambda}$ is given by (2.11) with $A = \{e^{i\underline{\lambda}} \cdot P, n = 0, 1, 2, ...\}$,

where **p** is the momentum operator of the electron. In order to have $\mathbf{p} = -i \nabla$ as a well defined self adjoint operator on \mathbb{R}^3 , we confine the electron by a smooth wall represented by a regular potential $U_{\Lambda}(x)$, $U_{\Lambda}(x) = 0$ if x in Λ and $U_{\Lambda}(x) \to \infty$ fast enough as $|x| \to \infty$. In this setting, the term with n impurities in $\langle e^{i\underline{\lambda}} \cdot P \rangle_{\Lambda}$ involves the following trace

Tr
$$\exp\left[-\beta\left((H_{\Lambda}^{n}(\mathbf{r}_{1},...,\mathbf{r}_{n})+U_{\Lambda})\right)\right]\exp[i\,\underline{\lambda}\,\cdot\,\mathbf{p}]$$

$$=\int d\mathbf{x}\,(\mathbf{x}\,|\exp\left[-\beta\left((H_{\Lambda}^{n}(\mathbf{r}_{1},...,\mathbf{r}_{n})+U_{\Lambda})\right)\right]\,|\,\mathbf{x}+\underline{\lambda})$$

$$=\int d\mathbf{x}\,\int d\mu_{\mathbf{x},\,0;\,\mathbf{x}+\underline{\lambda},\,\beta}^{\Lambda}(\underline{\omega})\prod_{j=1}^{n}\exp\left[-V(\mathbf{r}_{j},\,\underline{\omega})\right]$$
(7.2)

where $d\mu^{\Lambda}_{x,\,0;\,\,x\,+\,\lambda,\,\beta}$ (ω) is the conditional Wiener measure multiplied by the

weight factor
$$\exp\left(-\int\limits_0^\beta ds\ U_\Lambda\left(\underline{\omega}(s)\right)\right)$$
 of the wall.

Proceeding as in section II and IV, one can write $\langle e^{i\lambda} \cdot P \rangle_{\Lambda}$ as a ratio

$$\langle e^{i\underline{\lambda}} \cdot P \rangle_{\Lambda} = \frac{\widetilde{f}_{\Lambda}(\beta, z, \underline{\lambda})}{\widetilde{f}_{\Lambda}(\beta, z, 0)}$$
 (7.3)

with $f_{\Lambda}(\beta, z, \underline{\lambda})$ given by the analogue of (4.1)

$$\widetilde{f}_{\Lambda}(\beta, z, \underline{\lambda}) = \frac{1}{|\Lambda|} \int dx \int d\mu^{\Lambda}_{x, o; x + \underline{\lambda}, \beta}(\underline{\omega}) \frac{\Xi(\beta, z, \underline{\omega})}{\Xi_{o}(z)}$$
(7.4)

The functions $\Xi(\beta, z, \underline{\omega})$ and $\Xi_0(z)$ are the same as (4.2) and (2.19). The only difference with (4.1) is that the paths are no more closed, but start at x and end at $x + \underline{\lambda}$. The low activity expansion of (7.3) and the convergence proofs are then carried exactly in the same way as in section IV. In the thermodynamic limit the low activity series are similar to (5.1),

$$(2\pi\beta)^{3/2} \tilde{f}(\beta, z, \underline{\lambda}) = e^{-1\underline{\lambda} \cdot 1^{2/2}\beta} + w(\beta) e^{-\beta Eo} \operatorname{Tr} e^{-i\underline{\lambda} \cdot P} \left(e^{-\beta H^{1}} - e^{-\beta H^{0}} \right)$$

$$+ (2\pi\beta)^{3/2} \sum_{n=2}^{\infty} \left(z(\beta) \right)^{n} \tilde{f}^{n}(\beta, \underline{\lambda})$$

$$(7.5)$$

where the $\tilde{f}^n(\beta, \underline{\lambda})$ are given by the same expresssions as (4.33) and (4.37) with $d\mu_{\beta}(\underline{\omega})$ replaced by $d\mu_{x, o; x + \underline{\lambda}, \beta}(\underline{\omega})$. In the ionization equilibrium limit defined by

(3.13) with $w(\beta) \to w$, $\beta \to \infty$, the sum of all the terms of the series (7.5) with $n \ge 2$ vanish. The proof is the same as that of section V where one uses the lemma 4 and 5 for a general λ (see appendices C and D). Since $\exp(-\beta H^1) = |\psi_0\rangle < \psi_0| \exp(\beta E_0) + o(\exp(\beta E_0))$, one obtains

$$\lim_{\beta \to \infty} (2\pi\beta)^{3/2} \tilde{f}(\beta, z, \underline{\lambda}) = 1 + w \operatorname{Tr} e^{-i\underline{\lambda} \cdot p} |\psi_0\rangle \langle \psi_0|$$

$$= 1 + w \int d\underline{k} e^{-i\underline{\lambda} \cdot k} |\widetilde{\psi}_0(\underline{k})|^2$$
(7.6)

where $\tilde{\psi}_0$ (k) is the Fourier transform of the ground state wave function. Finally, taking (7.3), (7.6) and (3.14) into account leads to the final result for the momentum distribution in the ionization equilibrium limit

$$\lim_{\beta \to \infty} p(dk, \beta, z(\beta)) = \gamma_i \delta_0(dk) + (1 - \gamma_i) | \widetilde{\psi}_0(\underline{k}) |^2 dk$$
 (7.7)

One sees that the electron is in a statistical mixture of a free state and a bound state. With probability γ_i (the Saha coefficient) the electron is at rest* (i.e. in a plane wave with zero momentum), while with probability $1-\gamma_i$, its momentum distribution is that of the atomic ground state. This confirms that ionization equilibrium can be thought as a thermodynamical phase equilibrium of two different "species", the ionized electrons and the atoms.

It is also interesting to consider the spatial correlation of the electron at x with an impurity at r

$$\rho_{\Lambda}(x, r) = \frac{1}{\Xi_{\Lambda}(\beta, z)} \sum_{n=0}^{\infty} \frac{z^{n+1}}{n!} \int_{\Lambda} dr_{1} ... dr_{n} (x \mid \exp \left[-\beta H^{n}(r, r_{1}, ..., r_{n})\right] \mid x)$$
(7.8)

Since the electron is uniformly distributed in Λ , the conditional probability of finding an impurity at r when the electron is at x has density

$$g(x, r) = \lim_{|\Lambda| \to \infty} |\Lambda| \rho_{\Lambda}(x, r).$$

In the ionization equilibrium limit (3.13), only the lowest order term of the series (7.8) will contribute. Introducing the definition (2.21), using the result (3.14) and the fact that

$$\lim_{\beta \to \infty} e^{-\beta E_0} \left(x \mid \exp\left[-\beta H^1(r)\right] \mid x \right) = |\psi_0(r - x)|^2$$
(7.9)

one finds

^{*} It is at rest in the strict zero temperature limit. At a small non zero temperature, it would have a Maxwellian momentum distribution as shown by the first term in the r.h.s. of (7.5)

$$\lim_{\beta \to \infty} g(x, r) = \lim_{\beta \to \infty} \frac{z(\beta)}{f(\beta, z(\beta))} \left(x \mid \exp\left[-\beta H^{1}(r)\right] \mid x \right)$$

$$= \frac{w}{1+w} \mid \psi_{o}(r-x) \mid^{2} = \gamma_{b} \mid \psi_{o}(r-x) \mid^{2}$$
(7.10)

The interpretation of (7.10) is clear: the probability of finding an impurity at distance |x-r| of the electron is the probability of forming the atom times the configurational distribution in the ground state wave function.

This model of a single quantum mechanical particle interacting with a many body classical medium is used to discuss the properties of dilute electrons in molten salts or dense gases [13]. Here one studies by quantum molecular dynamics the adiabatic motion of the electronic wave function at zero temperature but finite density. The electron is found most of the time in a localized ground state. One observes occasional short time delocalization of the wave function corresponding to the jump of the electron to a neighboring place.

As far as the full quantum binding and ionisation equilibrium problem is concerned, one needs of course to introduce a many electron system with quantum mechanical protons and the Coulomb force. Then the lower bound (2.7) will be replaced by the stability of matter estimate expressed in an optimal form. The treatment of this general case necessitate the powerful technique developed by Fefferman in [4]. However, apart from the use of these highly non trivial tools, the results are the same as in the simple model studied in this paper. Ionisation equilibrium of real electrons and protons occurs in the same low density low temperature limit as that considered here. This is the subject of a forthcoming publication [15].

Appendix A. Proof of (3.3)

For each $N \in \mathbb{N}$ let V_N be the spherically symmetric attractive potential defined by

$$V_{N}(x) = \begin{cases} V(x) & \text{if } V(x) > -N \\ -N & \text{if } V(x) \le -N \end{cases}$$
(A.1)

 $V_N(x)$ is continuous and bounded. Let V_N^n be the corresponding n-impurity potential, that is

$$V_N^n(r_1, ..., r_n; x) = \sum_{j=1}^n V_N(r_j - x)$$

$$\| \, V^n - V^n_N \, \|_{K_3} = \sup_{x} \int |x - y|^{-1} \, |V^n(y) - V^n_N(y)| \, \, \mathrm{d}y$$

$$\leq n \sup_{\mathbf{X}} \int \frac{1}{|x-y|} \, | \, V(y) - V_N(y) \, | \, \, \mathrm{d}y \, = n \sup_{\mathbf{X}} \int \, \left[\left(\max(\,|\,\mathbf{x}\,|\,,\,|\,y\,|\,) \right) \right]^{-1} \, | \, V(y) - V_N(y) \, | \, \, \mathrm{d}y$$

$$\leq n \int \frac{|V(y) - V_N(y)|}{|y|} dy \leq n \int \frac{|V(y)|}{|y|} dy \tag{A.2}$$

In the third line of (A.2), we have used the fact that $\|V(y) - V_N(y)\|$ is spherically symmetric. Therefore, $\lim_{N\to\infty}\|V^n - V_N^n\|_{K_3} = 0$ by the dominated convergence

theorem since by (2.2) $\int \frac{|V(y)|}{|y|} dy < \infty.$ By theorem B.10.1, of [6] this implies that $\|e^{-tH}_N^n - e^{-tH}^n\|_{1,\infty} \to 0$ as $N \to \infty$ and thus

$$\left(x \mid \exp(-t H_N^n) \mid y\right) \rightarrow \left(x \mid \exp(-t H^n) \mid y\right)$$
 (A.3)

uniformly on compacts as $N \to \infty$. Now by Theorem 6.6 of [8], $(x \mid \exp(-tH_N^n) \mid y)$ is jointly continuous in x and y for all x and y in $\mid R^3$ and

$$\left(x \mid \exp(-t H_{N}^{n}) \mid y\right) = \int d\mu_{x, 0; y, t} (\underline{\omega}) \exp \begin{pmatrix} t \\ -\int_{0}^{t} ds \ V_{N}^{n}(\underline{\omega}(s)) \end{pmatrix}$$
(A.4)

Since the integrand of (A.4) is an increasing sequence, the monotone convergence theorem with respect to the measure $d\mu_{x,\,0;\,y,\,t}$ ($\underline{\omega}$) implies that $-\int\limits_0^t ds\ V_N^n(\underline{\omega}(s))$ has a limit for almost every ω as $N\to\infty$. The sequence $-V_N^n(\underline{\omega}(s))$ is also increasing, thus monotone convergence implies again

$$\lim_{N \to \infty} \int_{0}^{t} ds \ V_{N}^{n}(\underline{\omega}(s)) = \int_{0}^{t} ds \ V^{n}(\underline{\omega}(s))$$
(A.5)

as well as

$$\left(\mathbf{x} \mid \exp(-t \, \mathbf{H}_{N}^{n}) \mid \mathbf{y}\right) \to \int d\mu_{\mathbf{x}, \, 0; \, \mathbf{y}, \, \mathbf{t}} \, (\underline{\omega}) \exp\left(-\int_{0}^{t} ds \, V^{n} \, (\underline{\omega}(s))\right) \tag{A.6}$$

as $N \to \infty$ which proves (3.3).

Finite region case

Let

$$H_{N\Lambda}^{n} = -\frac{\hbar^{2}}{2m} \Delta_{\Lambda} + V_{N}^{n} (r_{1}, ..., r_{n}).$$
 (A.7)

By using Theorem 21.1 in [8] and the Trotter product formula as in Theorem 6.1 of [6] it follows that for almost all (x, y) in $\Lambda \times \Lambda$

$$\left(\mathbf{x} \mid \exp(-t \, \mathbf{H}_{N}^{n}) \mid \mathbf{y}\right) = \int d\mu_{\mathbf{x}, \, 0; \, \mathbf{y}, \, \mathbf{t}}(\underline{\omega}) \, \exp\left(-\int_{0}^{t} ds \, V_{N}^{n}(\underline{\omega}(s))\right) \, \mathbf{1}_{\Gamma_{\Lambda}^{t}}(\underline{\omega}) \qquad (A.8)$$

where $1_{\Gamma_{\Lambda}^{t}}$ is the characteristic function of the set (3.6). The right hand of (A.8) can be written as

$$\frac{1}{(2\pi t)^{3/2}} \exp\left(-|x-y|^2/2t\right) \cdot E\left\{ \exp\left(-\int_0^t ds \ V_N^n \left((1-\frac{s}{t})x + \frac{s}{t}y + \sqrt{t} \,\underline{\alpha} \,(\frac{s}{t})\right)\right) 1_{\Gamma_\Lambda^t} \left(1-\frac{s}{t}x + \frac{s}{t}y + \sqrt{t} \,\underline{\alpha} \,(\frac{s}{t})\right) \right\} \tag{A.9}$$

where $\underline{\alpha}$ is the Browninan bridge. Almost every $\underline{\alpha}$ is continuous and if $\underline{\alpha}$ is continuous, $(x, y) \in \Lambda \times \Lambda$ and $(1 - \frac{s}{t})x + \frac{s}{t}y + \sqrt{t}\underline{\alpha}(\frac{s}{t}) \in \Lambda$ for $0 \le s \le t$ then $d(\{(1 - \frac{s}{t})x + \frac{s}{t}y + \sqrt{t}\alpha(\frac{s}{t}): 0 \le s \le t\}), \partial\Lambda\} > 0$ so that

$$\lim_{(\mathbf{x'},\mathbf{y'})\to(\mathbf{x},\mathbf{y})} 1_{\Gamma_{\Lambda}^{t}} \left(\left(1 - \frac{s}{t}\right) \mathbf{x'} + \frac{s}{t} \mathbf{y'} + \sqrt{t} \underline{\alpha} \left(\frac{s}{t}\right) \right) = 1.$$

This combined with the continuity of V_N^n and the dominated convergence theorem implies as in Theorem 6.6 of [8] that $(x | \exp(-tH_N^n)|y)$ is jointly continuous in x and y for $(x, y) \in \Lambda \times \Lambda$.

It is easy to see that Theorem B 10.1 of [6] holds for $H_{N\Lambda}^{\ n}$ and H_{Λ}^{n} . The rest of the proof follows as above.

Appendix B. Proof of the formulas (4.7) and (4.8)

First we prove the following identity for any function F(1,...,k)

$$\sum_{r=0}^{n-k} \frac{(n-k)!}{r!(n-k-r)!} \int d1 \dots dn \ F(1,...,k) \chi_d^T (1,...,k \mid k+1 \mid ... \mid n-r) \chi_d(n-r+1,...,n)$$

$$= \int d1 \dots dn \ F(1,...,k) \chi_d (1,...,n)$$
(B.1)

Let $\mathcal{P}(A)$ denote the set of partitions of a set A, and let $J_k J'_k$ denote the two sets $\{q_k, q_{k+1}, ..., q_n\}$, $\{q_{k+1}, ..., q_n\}$ where $q_k = \{1, ..., k\}$, $q_{k+1} = \{k+1\}$, ..., $q_n = \{n\}$. One has

$$\chi_{\mathbf{d}}(1, ..., n) = \sum_{P \in \mathcal{P}(J_k)} \prod_{Q \in P} \chi_{\mathbf{d}}^{T}(Q)$$
 (B.2)

where χ_d^T (Q) is the hard core exclusion truncated with respect to the subsets q_i which constitute Q. Any $P \in \mathcal{P}(J_k)$ is of the form $(q_k \cup Q) \cup P'$ (here $(q_k \cup Q)$ is to be viewed as one set of the partition), with $Q = \emptyset$ or $Q \subset J'_k$ and $P' \in \mathcal{P}(J'_k \setminus Q)$. Thus we can write

$$\chi_{d}(1,...,n) = \sum_{r=0}^{n-k} \sum_{\substack{|Q|=n-k-r\\Q \in J'_{k}}} \chi_{d}^{T}(q_{k} \cup Q) \sum_{\substack{P' \in \mathcal{P}(J'_{k} \setminus Q)}} \prod_{\substack{Q' \in P'\\}} \chi_{d}^{T}(Q')$$
(B.3)

Inserting this formula in the right hand side of (B.1) we get

$$\int d1 \dots dn F(1,...,k) \chi_{d} (1,...,n)$$

$$= \sum_{r=0}^{n-k} \sum_{\substack{|Q|=n-k-r\\Q \subset J'_{k}}} \int d1 \dots dn F(1,...,k) \chi_{d}^{T}(q_{k} \cup Q) \sum_{P' \in \mathcal{P}(J'_{k} \setminus Q)} \prod_{Q' \in P'} \chi_{d}^{T} (Q')$$
(B.4)

In each integral of (B.4) we can relabel the integration variables ranging from k+1 to n so that the set Q consists of the elements $\{k+1,...,n-r\}$ and $J'_k Q = \{n-r+1,...,n\}$. Moreover, the number of sets satisfying the constraints $Q C \{k+1,...,n\}$ and |Q| = n-k-r is given by $\frac{(n-k)!}{(n-k-r)! \ r!}$. These remarks imply

$$\int d1 \dots dn F(1, \dots, k) \chi_{d}(1, \dots, n) = \sum_{r=0}^{n-k} \frac{(n-k)!}{(n-k-r)! r!} \int d1 \dots dn F(1, \dots, k)$$

$$\chi_{d}^{T}(1, \dots, k \mid k+1 \mid \dots \mid n-r) \sum_{P' \in \mathcal{P}(\{n-r+1, \dots, n\})} \prod_{Q' \in P'} \chi_{d}^{T}(Q')$$
(B.5)

which is exactly (B.1), since the sum over partitions \mathcal{P} ({n-r+1, ...,n}) equals χ_d (n-r+1,..., n).

To derive the expansion (4.7) we note that it is equivalent to

$$\Xi_{\Lambda}(\beta, z, \underline{\omega}) = \Xi_{\Lambda}^{0}(z) \left(1 + \sum_{n=1}^{+\infty} \frac{z^{n}}{n!} a_{n} \right)$$
 (B.6)

with $\Xi_{\Lambda}(\beta, z; \underline{\omega})$ and $\Xi_{\Lambda}^{0}(z)$ given by the series (4.4) and (4.5). Identifying the terms of order z^{n} in the two members of (B.6), we get an equation for the coefficients a_{n}

$$\int d1 \dots dn \, \chi_d(1, \dots, n) \prod_{j=1}^n f_j = \sum_{r=0}^n \frac{n!}{r!(n-r)!} \, a_{n-r} \int d1 \dots dr \, \chi_d(1, \dots, r)$$
 (B.7)

Thus it is sufficient to check that the coefficients a_n given by (4.8) satisfy the equation (B.7). Inserting (4.8) in the r.h.s. of (B.7), one has

$$\begin{split} &\sum_{r=0}^{n} \frac{n!}{r!(n-r)!} \ a_{n-r} \int d1 \dots dn \ \chi_{d}(1, ..., r) \\ &= \sum_{r=0}^{n} \frac{n!}{r!(n-r)!} \sum_{k=0}^{n-r} \frac{(n-r)!}{k!(n-r-k)!} \int d1 \dots dn \quad \prod_{j=1}^{k} (f_{j}-1) \\ &\cdot \chi_{d}^{T}(1, ..., k \mid k+1 \mid ... \mid n-r) \ \chi_{d}(n-r+1, ..., n) \\ &= \sum_{k=0}^{n} \frac{n!}{k!(n-k)!} \sum_{r=0}^{n-k} \frac{(n-k)!}{r!(n-k-r)!} \int d1 \dots dn \quad \prod_{j=1}^{k} (f_{j}-1) \\ &\cdot \chi_{d}^{T}(1, ..., k \mid k+1 \mid ... \mid n-r) \ \chi_{d}(n-r+1, ..., n) \end{split}$$

In the first equality we have relabeled (1 ... r) to (n-r+1 ... n). To get the second one, we have permuted the summations on $0 \le r \le n$ and $0 \le k \le n-r$. Now we

apply the identity (B.1) with $F(1... k) = \prod_{j=1}^{k} (f_j - 1)$

$$\sum_{r=0}^{n} \frac{n!}{r!(n-r)!} a_{n-r} \int d1 \dots dr \ \chi_{d}(1, \dots, r)$$

$$= \sum_{k=0}^{n} \frac{n!}{k!(n-k)!} \int d1 \dots dn \ \prod_{j=1}^{k} (f_{j}-1) \ \chi_{d}(1, \dots, n)$$
(B.9)

and with the help of the formula

$$\prod_{j=1}^{n} f_{j} = \sum_{k=0}^{n} \sum_{j_{1}...j_{k}}^{n} \prod_{i=1}^{k} (f_{j_{i}} - 1)$$
(B.10)

it is easy to see that the r.h.s. of (B.9) reduces to the l.h.s. of (B.7).

Appendix C. Proof of Lemma 4

To prove (5.13) we note that any $\underline{\omega} \in \mathcal{D}_{\mathbf{r}_1, \dots, \mathbf{r}_l}$ satisfies

$$\sup_{0 \le s \le \beta} |\underline{\omega}(s)| \ge |r_j| - a \tag{C.1}$$

for all j = 1, ..., l. It follows that for j = 2, ..., l

$$\sup_{0 \le s \le \beta} |\underline{\omega}(s)| \ge \frac{1}{2} |\mathbf{r}_{j}| + \frac{1}{2} |\mathbf{r}_{1}| - a$$

$$\ge \frac{1}{2} |\mathbf{r}_{j} - \mathbf{r}_{1}| - a \tag{C.2}$$

Thus the set $\mathcal{D}_{\mathbf{r}_1, \ldots, \mathbf{r}_l}$ is included in the intersection of the sets $\{\underline{\omega} \mid \underline{\omega}(0) = \underline{0} \text{ and } \sup_{s} |\underline{\omega}(s)| \ge \frac{1}{2} |\mathbf{r}_j - \mathbf{r}_1| - a\}$, $j = 2 \ldots l$, so that (5.13) is valid.

Now we prove a slightly more general version of (5.15) where $d\mu_{\beta}(\underline{\omega})$ is replaced by $d\mu_{o, \, o; \, \lambda \, \beta}(\underline{\omega})$. Let $\Delta_{x} = \{\underline{\omega} \, | \, \underline{\omega}(0) = 0 \text{ and } \sup_{0 \le s \le \beta} | \, \underline{\omega}(s) \, | \, > x \, \}$ for x > 0. The expectation of the set Δ_{x} in the conditional Wiener measure $d\mu_{o, \, o; \, \lambda \, \beta}$ can be expressed in terms of the usual expectation \mathcal{E} of Brownian motion b(s) by the formula [6].

$$\int_{\Delta_{\mathbf{X}}} d\mu_{\mathbf{o}, \, \mathbf{o}; \, \underline{\lambda} \, \beta}(\underline{\omega}) = \frac{e - \frac{|\underline{\lambda}|^2}{2\beta}}{(2\pi\beta)^{3/2}} \, \mathcal{E}(\mathbf{b} \mid \sup_{0 \le s \le 1} |s\,\underline{\lambda}| + \sqrt{\beta} \, (\mathbf{b}(s) - s\,\mathbf{b}(1))| > \times)$$

$$\leq \frac{e - \frac{|\underline{\lambda}|^2}{2\beta}}{(2\pi\beta)^{3/2}} \, \mathcal{E}(\mathbf{b} \mid 2\,\sqrt{\beta} \sup_{0 \le s \le 1} |\mathbf{b}(s)| > \times - |\underline{\lambda}|) \qquad (C.3)$$

The inequality (C.3) follows from

$$\sup_{0 \le s \le 1} |s \underline{\lambda} + \sqrt{\beta} (b(s) - s b(1))| \le |\underline{\lambda}| + 2\sqrt{\beta} \sup_{0 \le s \le 1} |b(s)|$$

By standard properties of the brownian motion (cf [6, p. 268]), we know that there exists positive constants C_1 and C_2 such that for any x > 0

$$\mathcal{L}(\mathbf{b} \mid \sup_{0 \le s \le 1} |\mathbf{b}(s)| > x) \le C_1 \exp(-C_2 x^2)$$
 (C.4)

If $\frac{x}{2} > |\lambda|$ then $x - |\lambda| > \frac{x}{2} > 0$, one obtains from (C.3), (C.4) for $\beta > 1$

$$\int_{\Delta_{\mathbf{x}}} d\mu_{\mathbf{o}, \mathbf{o}; \underline{\lambda} \beta}(\underline{\omega}) \le C_1 \exp\left(-\frac{C_2}{4\beta} \mathbf{x}^2\right)$$
 (C.5)

If $\frac{x}{2} \le |\underline{\lambda}|$, one has $\exp\left(-\frac{|\underline{\lambda}|^2}{2\beta}\right) \le \exp\left(-\frac{x^2}{4\beta}\right)$ and we obtain again (C.5) with $C_1 = C_2 = 1$, since the expectation in the right hand side of (C.3) does not exceed one. Thus, setting $K = \max(1, C_1)$ and $K = \min(1, C_2)$ we have for any x > 0 the inequality

$$\int_{\Delta_{\mathbf{X}}} d\mu_{\mathbf{o}, \, \mathbf{o}; \, \lambda \, \beta}(\underline{\omega}) \leq K \, \exp\left[-\frac{\bar{K}}{4\beta} \, x^2\right] \tag{C.6}$$

Noting that $\int d\mu_{o, o; \lambda \beta}(\underline{\omega}) \widetilde{\chi}_{a}(\underline{\omega}; r_{j} - r_{1}) \le 1$ if $\frac{1}{2} |r_{j} - r_{1}| \le a$ and $\beta > 1$, an application of (C.6) gives for all j = 2, ..., l

$$\int d\mu_{o, o; \lambda \beta}(\omega) \, \tilde{\chi}_{a}(\omega; r_{j} - r_{1}) \leq C_{a} \, \exp\left[-\frac{K}{4\beta} \left(\frac{1}{2} | r_{j} - r_{1} | - a\right)^{2}\right] \tag{C.7}$$

where C_a is an appropriate constant depending on a but independent of $\beta > 1$ and j. Moreover, using the inequality $\left(\frac{1}{2} | r_j - r_1| - a\right)^2 \ge \frac{1}{8} | r_j - r_1|^2 - a^2$ we deduce

$$\int d\mu_{o, o; \underline{\lambda}\beta}(\omega) \, \widetilde{\chi}_{a}(\omega; r_{j} - r_{1}) \leq C_{a} \, \exp\left[-\frac{\overline{K}}{32\beta} |r_{j} - r_{1}|^{2}\right]$$
 (C.8)

with another constant C_a . For any j = 2, ..., 1, we have

$$\int d\mu_{\mathbf{o}, \, \mathbf{o}; \, \underline{\lambda} \, \beta}(\underline{\omega}) \prod_{j=2}^{1} \widetilde{\chi}_{\mathbf{a}}(\underline{\omega}; \, \mathbf{r}_{j} - \mathbf{r}_{1}) \leq \int d\mu_{\mathbf{o}, \, \mathbf{o}; \, \underline{\lambda} \, \beta}(\underline{\omega}) \widetilde{\chi}_{\mathbf{a}}(\underline{\omega}; \, \mathbf{r}_{j} - \mathbf{r}_{1}) \tag{C.9}$$

Performing a product over j on the two sides of (C.9) and using (C.8), we conclude

$$\int d\mu_{o, o; \lambda \beta}(\underline{\omega}) \prod_{j=2}^{1} \widetilde{\chi}_{a}(\underline{\omega}; r_{j} - r_{1}) \leq C_{a} \prod_{j=2}^{1} \exp \left[-\frac{\overline{K}}{32\beta 1} |r_{j} - r_{1}|^{2} \right]$$
 (C.10)

which is (5.15) with D = $\frac{\overline{K}}{321}$.

Appendix D. Proof of Lemma 5

We prove a slightly more general form of the lemma 5 estimating Tr $|V^n| \exp[-\beta H^n] \exp(i \lambda p)$ with $\exp(i \lambda p)$ the unitary operator of space translations (p is the momentum operator). Using the semi-group property of $\exp[-\beta H^n]$ and applying the lemma 1, we note that for $0 < \epsilon < \beta$

$$\begin{split} &(x_{1} \mid \exp[-\beta H^{n}] \mid x_{2}) = \\ &\int dy_{1} \int dy_{2} (x_{1} \mid \exp[-\frac{\varepsilon}{2} H^{n}] \mid y_{1}) (y_{1} \mid \exp[-(\beta - \varepsilon) H^{n}] \mid y_{2}) (y_{2} \mid \exp(-\frac{\varepsilon}{2} H^{n}) \mid x_{2}) \\ &\leq A^{2} e^{B\varepsilon} \int dy_{1} \int dy_{2} (x_{1} \mid \exp[-\varepsilon H^{o}] \mid y_{1}) (y_{1} \mid \exp[-(\beta - \varepsilon) H^{n}] \mid y_{2}) \\ &(y_{2} \mid \exp[-\varepsilon H^{o}] \mid x_{2}) = A^{2} e^{B\varepsilon} (x_{1} \mid \exp[-\varepsilon H^{o}] \exp[-(\beta - \varepsilon) H^{n}] \exp[-\varepsilon H^{o}] \mid x_{2}) \end{split} \tag{D.1}$$

Hence one finds

$$\begin{split} &\operatorname{Tr} \mid V^{n} \mid \exp[-\beta \, H^{n}] \exp\left(\mathrm{i} \, \underline{\lambda} \cdot p\right) = \int \, dx \, \mid V^{n} \mid^{1/2} (x) \, (x \mid \exp[-\beta \, H^{n}] \mid x - \underline{\lambda}) \mid V^{n} \mid^{1/2} (x) \\ & \leq A^{2} \, e^{B\epsilon} \operatorname{Tr} \left\{ \mid V^{n} \mid^{1/2} \, \exp[-\epsilon \, H^{0}] \exp[-(\beta - \epsilon) H^{n}] \exp[-\epsilon \, H^{0}] \exp\left(\mathrm{i} \, \underline{\lambda} \cdot p\right) \mid V^{n} \mid^{1/2} \right\} \\ & \leq A^{2} \, e^{B\epsilon} \, \left\| \mid V^{n} \mid^{1/2} \, \exp[-\epsilon \, H^{0}] \exp[-\frac{1}{2} (\beta - \epsilon) H^{n}] \, \right\|_{2} \\ & \quad \left\| \mid V^{n} \mid^{1/2} \, \exp[-\epsilon \, H^{0}] \exp\left(\mathrm{i} \, \underline{\lambda} \cdot p\right) \exp[-\frac{1}{2} (\beta - \epsilon) H^{n}] \, \right\|_{2} \\ & \leq A^{2} \, e^{B\epsilon} \exp[-(\beta - \epsilon) \operatorname{Inf} \operatorname{spec} H^{n}] \, \left\| \mid V^{n} \mid^{1/2} \exp[-\epsilon \, H^{0}] \, \right\|_{2}^{2} \end{split} \tag{D.2}$$

To obtain (D.2), we have successively used (D.1), $|\text{Tr CD}^*| \leq |\text{Cl}_2|\text{Dl}_2$, $|\text{I.l}_2|$ being the Hilbert-Schmidt norm, and $|\text{CDl}_2| \leq |\text{Cl}_2|\text{Dl}$. An explicit calculation of the Hilbert-Schmidt norm gives

$$\begin{split} & \| \| V^n \|^{1/2} \exp[-\epsilon H^0] \|_2^2 = \frac{1}{(2\pi\epsilon)^3} \int dx \int dy \| V^n \| (x) \exp\left[-\frac{\|x-y\|^2}{\epsilon}\right] \\ & = \| V^n \|_1 \frac{1}{(4\pi\,\epsilon)^{3/2}} \le \frac{n}{(4\pi\,\epsilon)^{3/2}} \| V \|_1 \end{split}$$

leading to

$$\operatorname{Tr} \, | \, V^n \, | \, \exp[-\beta \, H^n] \, \exp\left(\mathrm{i} \, \underline{\lambda} \, . \, \, p\right) \leq C_{\epsilon} \, \left\| \, V \, \right\|_1 \, \exp\left[-\left(\beta - \epsilon\right) \, \inf \operatorname{spec} \, H^n\right]$$

with $C_{\epsilon}=\frac{n\,A}{(4\,\pi\,\epsilon)^{3/2}}\,\,e^{B\epsilon}.$ The result of the lemma corresponds to the special case $\underline{\lambda}=0.$

Now we prove that

$$\lim_{\beta \to +\infty} e^{-\beta E_0} \operatorname{Tr} \exp (i \underline{\lambda} \cdot p) \left(\exp[-\beta H^1] - \exp[-\beta H^0] \right) = \int dk \, e^{i \underline{\lambda} \cdot k} |\widetilde{\psi}_0(\mathbf{k})|^2 \tag{D.3}$$

where $\widetilde{\psi}_0$ is the Fourier transform of the ground state wave function of the one impurity hamiltonian H^1 . This formula justifies (2.27) taking $\underline{\lambda} = 0$ in (D.3), and it is actually used in the section VII for a general $\underline{\lambda}$. Since we know (section III) that $\exp[-\beta H^1] - \exp[-\beta H^0]$ is trace class we can write

$$\begin{split} &e^{-\beta Eo} \text{ Tr exp (i } \underline{\lambda} \cdot p) \left(\exp[-\beta H^1] - \exp[-\beta H^0] \right) = \int dk \, e^{i \, \underline{\lambda} \cdot k} \, |\, \widetilde{\psi}_o(k) \, |^2 \\ &- e^{-\beta Eo} \int dk \, e^{i \, \underline{\lambda} \cdot k} \, \exp \! \left[-\beta \, \frac{|\, k \, |^2}{2} \right] \, |\, \widetilde{\psi}_o(k) \, |^2 \\ &+ e^{-\beta Eo} \text{ Tr exp (i } \underline{\lambda} \cdot p) \, Q_o \left(\exp[-\beta H^1] - \exp[-\beta H^0] \right) \end{split} \tag{D.4}$$

where Q_o is the projector on the orthogonal complement of the ground state. When $\beta \to +\infty$ the second term on the right hand side of (D.4) vanishes so it remains to estimate the last term :

$$\| \exp (i \lambda \cdot p) Q_{o} \left(\exp[-\beta H^{1}] - \exp[-\beta H^{0}] \right) \|_{1}$$

$$\leq \int_{\beta/2}^{\beta/2} ds \| Q_{o} e^{-sH^{1}} V e^{-(\beta-s)H^{0}} \|_{1} + \int_{\beta/2}^{\beta} ds \| Q_{o} e^{-sH^{1}} V e^{-(\beta-s)H^{0}} \|_{1}$$

$$\leq \int_{\beta/2}^{\beta} ds \| Q_{o} e^{-sH^{1}} \| V \exp(-\frac{\beta}{2}H^{0}) \|_{1} +$$

$$+ \int_{\beta/2}^{\beta} ds \| Q_{o} \exp\left[-(s-\frac{\beta}{2}H^{1})\right] \| Q_{o} \exp(-\frac{\beta}{2}H^{1}) V \|_{1}$$

$$\leq \frac{\beta}{2} \exp(-\frac{\beta}{2}(-Eo + \delta)) \| V \exp(-\frac{\beta}{2}H^{0}) V \|_{1}$$

$$+ \exp(-\frac{\beta}{2}(-Eo + \delta)) \| Q_{o} \exp(-\frac{\beta}{2}H^{1}) V \|_{1}$$

$$(D.5)$$

To obtain (D.5) we have first used the integral equation for the semi group and the bound $\|CD\|_1 \le \|C\| \|D\|_1$ together with the semi group property. For the

last estimate we recall that the eigenvalue $-E_o$ is isolated hence it is possible to find $\delta > 0$ such that $\|Q_o \exp(-tH^1)\| \le \exp(-t(-E_o + \delta))$. Moreover, for $\beta > 1$ we have

$$\| V \exp(-\frac{\beta}{2}H^{0}) \|_{1} = \| V \exp(-\frac{1}{2}H^{0}) \exp\left[(-(\frac{\beta-1}{2})H^{0})\right] \|_{1} \le \| V \exp(-\frac{1}{2}H^{0}) \|_{1}$$
(D.6)

and

$$\begin{split} & \| Q_{o} \exp(-\frac{\beta}{2} H^{1}) \ V \ \|_{1} \leq \| Q_{o} \exp\left[(-(\frac{\beta-1}{2}) H^{1})\right] \| \ \| \exp(-\frac{1}{2} H^{1}) \ V \ \|_{1} \\ & \leq \exp\left[-(\frac{\beta-1}{2}) (-E_{o} + \delta)\right] \| \exp(-\frac{1}{2} H^{1}) \ V \ \|_{1} \end{split} \tag{D.7}$$

Finally, (D.5), (D.6), (D.7) lead to

$$\begin{split} & e^{-\beta Eo} \operatorname{Tr} \exp (i \ \underline{\lambda} \cdot p) \ Q_o \left(\exp[-\beta H^1] - \exp[-\beta H^0] \right) \\ & \leq \frac{\beta}{2} \ \exp(-\frac{\beta}{2} (-E_o + \delta)) \ \| \ V \ \exp(-\frac{1}{2} H^0) \ \|_1 \\ & + \frac{\beta}{2} \ e^{-\beta \delta} \exp(\frac{1}{2} (-E_o + \delta)) \ \| \ \exp(-\frac{1}{2} H^1) \ V \ \|_1 \end{split} \tag{D.8}$$

so that the last term of (D.4) vanishes when $\beta \to \infty$.

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