Atomic correlations and van der Waals forces

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Abstract. The effective potential between two electron-proton pairs at distance r in thermal equilibrium with a weakly coupled classical plasma is calculated and shown to decay as r^{-6} for all temperatures and densities. In the atomic regime (low temperature and low density), it reduces to the usual van der Waals potential computed for hydrogen atoms in their ground states. In the limit of full ionization (high temperature), it is given by the r^{-6}-correlation that also exists between unbound charges. The model demonstrates that the conventional van der Waals forces and the algebraic tails generally found in the quantum Coulombic correlations have the same common origin in the intrinsic quantum fluctuations of the charges.

1   Introduction and results

The simplest standard text book calculation of van der Waals forces is well known [1]. One considers two hydrogen atoms in their ground state, with infinitely haevy nuclei located in $\mathbf{r}_a$ and $\mathbf{r}_b$. The total hamiltonian is the sum of the individual atomic hamiltonians H_a, H_b, and of the residual Coulomb interaction V

$$
\begin{aligned}
H &= H_a + H_b + V, \quad H_a = \frac{|\mathbf{p}_1|^2}{2m} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_a|}, \quad H_b = \frac{|\mathbf{p}_2|^2}{2m} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_b|} \\
V &= e^2 \left(\frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_b|} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_a|} \right)
\end{aligned} \tag{1.1}
$$

where $\mathbf{p}_i, \mathbf{r}_i$, $i = 1, 2$, are the momentum and position operators of the two electrons. For large atomic separation $r = |\mathbf{r}_a - \mathbf{r}_b| \to \infty$, V behaves as a dipolar potential

$$V \simeq \frac{e^2}{r^3} V_{\text{dip}}, \qquad V_{\text{dip}} = \mathbf{x}_1 \cdot \mathbf{x}_2 - 3(\mathbf{x}_1 \cdot \hat{\mathbf{r}})(\mathbf{x}_2 \cdot \hat{\mathbf{r}}) \qquad (1.2)$$

where $\mathbf{x}_1 = \mathbf{r}_1 - \mathbf{r}_a$, $\mathbf{x}_2 = \mathbf{r}_2 - \mathbf{r}_b$ are the relative electronic coordinates and $\hat{\mathbf{r}} = \frac{\mathbf{r}}{r}$. The two atoms are supposed to be in their ground states $\psi_{a,0}$, $\psi_{b,0}$ with energy E_0. Then the van der Waals potential Φ_w is obtained by treating V as a second order perturbation of the ground state energy of $H_a + H_b$ giving

$$\Phi_w(r) = \frac{C_w}{r^6} \qquad (1.3)$$

with

$$C_w = e^4 \sum_{\text{intermediate states}} \frac{|(\psi_{a,0} \otimes \psi_{b,0}, V_{\text{dip}} \psi_{a,i} \otimes \psi_{b,j})|^2}{2E_0 - E_i - E_j} < 0 \qquad (1.4)$$

The sum runs on all excited states $\psi_{a,i} \otimes \psi_{b,j}$, $(i, j) \neq (0, 0)$, of the two atoms (including the continuous spectrum).

This derivation raises several questions. First of all, the van der Waals forces are introduced phenomenologically in the realm of classical statistical mechanics to study equilibrium properties of atomic or molecular phases. It would therfore be advisable to derive them also in a non vanishing temperature state. But then one must immediately face the fact that a finite number of protons and electrons do not form atoms in an infinite but otherwise empty space if the temperature $T = (k_B \beta)^{-1}$ is not zero. Indeed, because of the large phase space available for ionized states, dissociation always wins over binding. In order to see the formation of hydrogen atoms, one needs to consider a non-zero density electron-proton gas in an appropriate low density and low temperature limit (the atomic limit) as shown in the works of Fefferman [2], Conlon, Lieb and Yau [3], and Graf and Schenker [4]. In the atomic limit, one lowers the temperature while keeping the chemical potentials fixed and negative. The choice of the chemical potentials determines a certain energy-entropy balance which in turn selects the formation of some specific bound entities as $T \to 0$. Clearly, from a more fundamental view point, the van der Waals forces originate from the correlations between the atoms that are formed in this limit. This leads in turn to another problem: if these forces have to be computed into a non vanishing density medium (containing also free charges), how will possible screening effects modify their range and their intensity?

In this note, we adress some of these questions in a simpler setting than the full electron-proton gas, treating only two electrons quantum mechanically. Then, in view of the above remarks, one can think of two ways for deriving van der Waals forces when the temperature is different from zero. One could consider the thermal state of our two atoms constrained to stay into a finite space region of volume $\sim \exp(\delta\beta)$ for a suitable $\delta > 0$, representing the effective available space per atom at low atomic density. One can also immerse the two electron-proton pairs into an infinitely extended medium constituted by a weakly coupled classical plasma in thermal equilibrium. The latter model, which is the object of our study, is a truly many-body Coulomb system. Although a simplification occurs from the fact that

only two specified electrons can undergo the quantum mechanical binding process, it already captures some significant features of the general situation.

The model is introduced in section 2 with the help of the Feynman-Kac functional integral: it is an extended version of a simpler setting discussed in sec.VII of [5] where binding mechanisms were not considered. An effective (temperature and density dependent) potential $\phi_{\beta,\rho}(r)$ between the two electron-proton pairs is defined in section 3, with ρ the density of the classical plasma. We establish the following points:

(i) For all β and $\rho > 0$ such that the plasma is in the Debye-Hückel regime

$$\Phi_{\beta,\rho}(r) \simeq \frac{C(\beta,\rho)}{r^6}, \quad r \to \infty, \quad C(\beta,\rho) < 0 \tag{1.5}$$

(ii) For any fixed ρ,

$$C(\beta,\rho) \simeq -\beta^3 \frac{\hbar^4 e^4}{240 m^2}, \quad \beta \to 0 \tag{1.6}$$

(iii) There is $\delta > 0$ such that for $\rho = \exp(-\delta\beta)$

$$\lim_{\beta \to \infty} C(\beta,\rho) = C_w \tag{1.7}$$

where C_w is the van der Waals coefficient (1.4).

One retrieves in point (i) the result that, in an homogeneous phase, the correlation between two quantum charges decays as r^{-6} irrespective of the fact that these charges belong to bound entities or not. This was shown semi-classically in [5] and more generally in [6]. The effective potential is non vanishing and attractive at large distances in the whole range of temperatures $0 < \beta < \infty$. In the high temperature limit (point (ii)) one recovers the correlation that always exists between free (unbound) charges as a consequence of their quantum nature. In the low temperature and low density limit, the amplitude $C(\beta,\rho)$ tends to the usual van der Waals coefficient C_w calculated for atoms in their ground states in empty space, as it should be (point (iii)). One can therefore say in a generalized sense that there exist van der Waals forces between quantum charges whether they are bound in atoms, or partially and even fully ionized. From a conceptual view point, there is no qualitative distinction between the traditional van der Waals forces, attributed to the interaction between atomic dipole moments, and the general non exponential r^{-6} decay of the correlation between quantum charges. As the Feynman-Kac formalism exemplifies it, both aspects have their common origin in the same basic quantum fluctuations. The difference is only quantitative. In the atomic regime, the amplitude $C(\beta,\rho)$ has an appreciable value close to C_w whereas it becomes vanishingly small at high temperature.

The low temperature and low density limit requires more care since screening effects desappear as the density goes to zero and one must control the long range of the Coulomb potential. This is studied in some details in section 4 and in the appendix. The subject of this work is also treated in part in [7].

2 Two electron-proton pairs in a classical plasma

We have again two quantum mechanical electrons $(\mathbf{p}_i, \mathbf{r}_i)$, $i = 1, 2$, in presence of two classical protons at $\mathbf{r}_a$ and $\mathbf{r}_b$. In addition these particles interact with a configuration Ω of a classical plasma. In the sequel it will not be necessary to specify the detailed constitution of this classical plasma (it can be a jellium or a multicomponent system) except for the following general properties. Its charges (of magnitude e_0) are assumed to be extended to insure classical stability. Moreover, this plasma is homogeneous with density ρ and weakly coupled: its dimensionless coupling parameter

$$\Gamma = \kappa \beta e_0^2, \qquad \kappa = \text{inverse Debye length} = \sqrt{4\pi e_0^2 \beta \rho} \tag{2.1}$$

is small. In particular, we will consider the high temperature limit

$$\rho \text{ fixed}, \quad \beta \to 0 \tag{2.2}$$

and the low temperature and low density limit

$$\rho = \exp(-\delta\beta), \quad \delta > 0, \quad \beta \to \infty \tag{2.3}$$

Under these conditions, $\Gamma \to 0$ and the theorems on Debye screening apply [8]: any classical external charge distribution is screened exponentially fast in the plasma.

The total hamiltonian for the two electrons in presence of the protons at $\mathbf{r}_a$, $\mathbf{r}_b$ and of the configuration Ω is[1]

$$H(\mathbf{r}_a, \mathbf{r}_b, \Omega) = \frac{|\mathbf{p}_1|^2}{2m} + \frac{|\mathbf{p}_2|^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b, \Omega) \tag{2.4}$$

where

$$U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b, \Omega) = \sum_{i=1}^{2} U(\mathbf{r}_i, \mathbf{r}_a, \mathbf{r}_b, \Omega) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_a - \mathbf{r}_b|} + U_0(\Omega) \tag{2.5}$$

is the sum of all Coulombic interactions. In (2.5), $U(\mathbf{r}_i, \mathbf{r}_a, \mathbf{r}_b, \Omega)$ is the potential energy of a single electron with all the other classical charges and $U_0(\Omega)$ is the self-energy of the plasma.

In order to define the effective potential between atoms we consider first the four-point correlation function of our two protons and two electrons in thermal equilibrium with the plasma enclosed in a region Λ

$$\rho_\Lambda(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b) = \frac{1}{Z_{0,\Lambda}} \int_\Lambda d\Omega \langle \mathbf{r}_1, \mathbf{r}_2 | \exp(-\beta H(\mathbf{r}_a, \mathbf{r}_b, \Omega)) | \mathbf{r}_1, \mathbf{r}_2 \rangle \tag{2.6}$$

Here $\langle \cdots \rangle$ is the diagonal part of the Gibbs statistical operator for the electrons, $\int_\Lambda d\Omega$ is the phase space integration on the coordinates of the classical plasma and $Z_{0,\Lambda} = \int_\Lambda d\Omega \exp(-\beta U_0(\Omega))$ the corresponding partition function. Since we will be only

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[1]A quantum mechanical treatment of the protons would not change the findings of this paper.

interested in large distance behaviours, we have omitted the electronic exchange term[2]. One can also interprete $-\beta^{-1} \ln \rho_\Lambda(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ as the excess free energy (without exchange effects) due to the immersion of the electrons and protons in the plasma.

To analyse $\rho_\Lambda(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ it is very useful to use the Feynman-Kac formalism and to write it in the Brownian bridge representation [9], [5]. In this representation, a quantum point particle at $\mathbf{r}$ becomes a closed path starting and ending at $\mathbf{r}$

$$\mathbf{r} + \lambda \xi(s), \ 0 \leq s \leq 1, \quad \xi(0) = \xi(1) = 0, \quad \lambda = \hbar\sqrt{\frac{\beta}{m}} \tag{2.7}$$

where λ is the thermal de Broglie length and $\xi(s)$ is a closed dimensionless path (the Brownian bridge) at the origin. The Brownian bridge is distributed according to the Gaussian measure $D(\xi)$ with covariance

$$\int D(\xi)\xi_\mu(s)\xi_\nu(t) = \delta_{\mu,\nu}(\min(s,t) - st), \quad \mu, \nu = 1, 2, 3 \tag{2.8}$$

Thus one can view a quantum charge as a classical charged filament $(\mathbf{r}, \xi)$, where the random shape ξ of the filament plays the role of an internal degree of freedom. In the Brownian bridge representation the potential energy $U(\mathbf{r}_i, \mathbf{r}_a, \mathbf{r}_b, \Omega)$ of a single electron becomes

$$\int_0^1 ds U(\mathbf{r}_i + \lambda \xi(s), \mathbf{r}_a, \mathbf{r}_b, \Omega) \tag{2.9}$$

and is equal to the classical electrostatic energy of a filament together with the charges at $\mathbf{r}_a, \mathbf{r}_b, \Omega$. However the electronic repulsion becomes

$$\int_0^1 ds \frac{e^2}{|\mathbf{r}_1 + \lambda \xi_1(s) - \mathbf{r}_2 - \lambda \xi_2(s)|} \tag{2.10}$$

which *is not equal* to the genuine Coulomb energy of two charged filaments. The later energy would be

$$\int_0^1 ds_1 \int_0^1 ds_2 \frac{e^2}{|\mathbf{r}_1 + \lambda \xi_1(s_1) - \mathbf{r}_2 - \lambda \xi_2(s_2)|} \tag{2.11}$$

since every element of charge $\xi_1(s_1)ds_1$ of the first filament has to interact with every element $\xi_2(s_2)ds_2$ of the other by the Coulomb law [3]. Hence we can write the matrix element in (2.6) as

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \exp(-\beta H(\mathbf{r}_a, \mathbf{r}_b, \Omega)) | \mathbf{r}_1, \mathbf{r}_2 \rangle =$$

$$\left(\frac{1}{2\pi\lambda^2}\right)^3 \int D(\xi_1) D(\xi_2) \exp\left(-\beta U_{\mathrm{cl}}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \mathbf{r}_a, \mathbf{r}_b, \Omega) - \beta W(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2)\right) \tag{2.12}$$

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[2]In the Feynman-Kac representation introduced below, the exchange matrix element $\langle \mathbf{r}_1, \mathbf{r}_2 | \exp(-\beta H(\mathbf{r}_a, \mathbf{r}_b, \Omega)) | \mathbf{r}_2, \mathbf{r}_1 \rangle$ has a Gaussian factor $\exp(-\frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{2\lambda^2})$ that does not contribute when the electrons are far apart.

[3]In (2.9), (2.10) and (2.11) the self-energy of a filament is not included.

where U_{cl} is the genuine total electrostatic energy of the filaments and of the charges, and W is a quantum correction (the difference of (2.10) and (2.11)) accounting for the quantum mechanical nature of the two electrons

$$W(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2) = e^2 \int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1) \frac{1}{|\mathbf{r}_1 + \lambda\xi_1(s_1) - \mathbf{r}_2 - \lambda\xi_2(s_2)|} \quad (2.13)$$

Finally, integrating on the configurations of the plasma, dividing by $Z_{0,\Lambda}$ and taking the thermodynamic limit yields

$$\rho(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b) = \lim_{\Lambda \to \infty} \rho_\Lambda(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b) =$$

$$\left(\frac{1}{2\pi\lambda^2}\right)^3 \int D(\xi_1) D(\xi_2) e^{-\beta W(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2)} f(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \mathbf{r}_a, \mathbf{r}_b) \quad (2.14)$$

where

$$f(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \mathbf{r}_a, \mathbf{r}_b) = \lim_{\Lambda \to \infty} \frac{1}{Z_{0,\Lambda}} \int_\Lambda d\Omega \exp(-\beta U_{\text{cl}}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \mathbf{r}_a, \mathbf{r}_b, \Omega)) \quad (2.15)$$

is now the genuine classical correlation of filaments and charges immersed in the plasma. In the same way, one can introduce 3 and 2 point-correlations, for instance the single electron-proton pair correlation

$$\rho(\mathbf{r}, \mathbf{r}_a) = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \int D(\xi) f(\mathbf{r}, \xi, \mathbf{r}_a) \quad (2.16)$$

To make the model completely definite, we write the classical correlations f in the Debye-Hückel approximation. One has in particular (see for instance appendix G of [5])

$$f(\mathbf{r}, \xi, \mathbf{0}) = \exp(-\beta F(\xi)) \exp\left(\beta e^2 \int_0^1 ds V_\kappa(\mathbf{r} + \lambda\xi(s))\right) \quad (2.17)$$

with

$$F(\xi) = \frac{e^2}{2} \int_0^1 ds_1 \int_0^1 ds_1 (V_\kappa(\lambda|\xi(s_1) - \xi(s_2)|) - V(\lambda|\xi(s_1) - \xi(s_2)|)) \quad (2.18)$$

and

$$V_\kappa(r) = \frac{e^{-\kappa r}}{r} \quad (2.19)$$

is the Debye potential. In fact, the Debye-Hückel expression (2.17) becomes asymptotically exact as the coupling Γ tends to zero [10].

The quantum interaction term W occurs only in correlations involving the two electrons. For fixed filament shapes it is a long range dipolar interaction

$$W(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2) \simeq e^2 \int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1)$$

$$\times (\lambda\xi_1(s_1) \cdot \nabla_{\mathbf{r}_1})(\lambda\xi_2(s_2) \cdot \nabla_{\mathbf{r}_2}) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right), \quad |\mathbf{r}_1 - \mathbf{r}_2| \to \infty \quad (2.20)$$

that will eventually be responsible for the van der Waals forces.

3   The effective potential

To investigate the large distance behaviour of $\rho(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ it is appropriate to consider the corresponding fully truncated correlation $\rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ defined in the usual way. Since we are not interested into the individual electronic positions but only in the large separation of the electron-proton pairs, we integrate over the electronic variables $\mathbf{r}_1$ and $\mathbf{r}_2$ and define the dimensionless normalized pair correlation

$$G(r) = \frac{1}{2A^2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b), \quad A = \int d\mathbf{r} \rho_T(\mathbf{r}, \mathbf{0}) \tag{3.1}$$

Because of translation invariance, $G(r)$ depends only on the separation $r = |\mathbf{r}_b - \mathbf{r}_a|$ of the center of mass of the pairs. It is normalized by the product A^2 of single pairs correlations and the factor $1/2$ takes into account that the electrons, treated here as identical particles, can be found in the neighborhood of either one of the protons.

We define the effective (temperature and density dependent) potential $\Phi_{\beta,\rho}(r)$ between the two electron-proton pairs by

$$G(r) = \exp(-\Phi_{\beta,\rho}(r)) - 1 \simeq -\beta \Phi_{\beta,\rho}(r), \quad r \to \infty \tag{3.2}$$

In order to determine its asymptotic behaviour, we express $\rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ in terms of the classical truncated correlations f_T of charges and filaments in the plasma with the abbreviated notation $1 = (\mathbf{r}_1, \xi_1), \ldots, a = \mathbf{r}_a, \ldots$. After some algebra one finds

$$\rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b) = \left(\frac{1}{2\pi\lambda^2}\right)^3 \int D(\xi_1) D(\xi_2)$$

$$\{(\exp(-\beta W(1,2)) - 1)(f_T(1,a) f_T(2,b) + f_T(1,b) f_T(2,a)) +$$

$$(\exp(-\beta W(1,2)) - 1)(f(1) f_T(2,a,b) + f(2) f_T(1,a,b)) + f_T(1,2,a,b)\} \tag{3.3}$$

In (3.3) the f_T are genuine truncated classical correlations in the Debye regime: they cluster exponentially fast as particles are taken far apart. Therefore the dominant contribution to $\rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b)$ as $|\mathbf{r}_b - \mathbf{r}_a| \to \infty$ comes from the first part in the integrand (3.3) and one concludes that (using the symmetry $W(1,2) = W(2,1)$)[4]

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_a, \mathbf{r}_b) \simeq$$

$$2 \left(\frac{1}{2\pi\lambda^2}\right)^3 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int D(\xi_1) D(\xi_2) (\exp(-\beta W(1,2)) - 1) f_T(1,a) f_T(2,b)$$

$$= 2 \left(\frac{1}{2\pi\lambda^2}\right)^3 \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int D(\xi_1) D(\xi_2) f_T(\mathbf{x}_1, \xi_1, 0) f_T(\mathbf{x}_2, \xi_2, 0)$$

$$\times \ (\exp(-\beta W(\mathbf{x}_1 - \mathbf{x}_2 - \mathbf{r}, \xi_1, \xi_2)) - 1), \quad r \to \infty \tag{3.4}$$

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[4]One can check that integrations one the electronic variables are convergent.

In the last integral of (3.4) one has introduced the relative electronic coordinates $\mathbf{x}_1 = \mathbf{r}_1 - \mathbf{r}_a$, $\mathbf{x}_2 = \mathbf{r}_2 - \mathbf{r}_b$ and $\mathbf{r} = \mathbf{r}_b - \mathbf{r}_a$, and from (2.17)

$$f_T(\mathbf{x}, \xi, 0) = \exp(-\beta F(\xi)) \left(\exp\left(\beta e^2 \int_0^1 ds V_\kappa(\mathbf{x} + \lambda\xi(s)) \right) - 1 \right) \tag{3.5}$$

Expanding $\exp(-\beta W) - 1 = -\beta W + \frac{1}{2}(\beta W)^2 + \cdots$ in (3.4), let us first show that the term linear in W does not contribute to the asymptotic behaviour. Indeed, the joint measure $d\mathbf{x}D(\xi)$ is invariant under the simultaneous rotations of $\mathbf{x}$ and of the filament shape in three dimensional space. The same is true for $f_T(\mathbf{x}, \xi, 0)$ in the homogeneous classical plasma. Hence introducing the multipolar expansion of the Coulomb potential in W, i.e.

$$W(\mathbf{x}_1 - \mathbf{x}_2 - \mathbf{r}, \xi_1, \xi_2) = e^2 \int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1)$$

$$\times \sum_{k,l=1}^\infty \frac{(-1)^k}{k!\,l!} [(\mathbf{x}_1 + \lambda\xi_1(s_1)) \cdot \nabla_r]^k [(\mathbf{x}_2 + \lambda\xi_2(s_2)) \cdot \nabla_r]^l \left(\frac{1}{r} \right) \tag{3.6}$$

one sees the occurence of integrals

$$\int d\mathbf{x} \int D(\xi) f_T(\mathbf{x}, \xi, 0) [(\mathbf{x} + \lambda\xi(s)) \cdot \nabla_r]^k \left(\frac{1}{r} \right), \quad k \geq 1 \tag{3.7}$$

In view of these symmetry considerations, the above integral vanishes if k is odd, and when k is even it is necessarily proportional to $(\nabla_r^2)^{k/2} \left(\frac{1}{r} \right) = 0$, $r \neq 0$. Since $f_T(\mathbf{x}, \xi, 0)$ is an exponentially decreasing function of $\mathbf{x}$ and all moments of the Gaussian measure $D(\xi)$ are finite, one concludes that the term linear in W decays faster than any inverse power of r. The leading behaviour is therefore determined by the quadratic term keeping only the dipole interaction in (3.6). Hence we obtain from (3.4) and (3.6) the asymptotic form of the effective potential

$$\Phi_{\beta,\rho}(r) \simeq -\beta^{-1} G(r) \simeq \frac{C(\beta, \rho)}{r^6}, \quad r \to \infty \tag{3.8}$$

with

$$C(\beta, \rho) = -\frac{\beta e^4}{2A^2} \left(\frac{1}{2\pi\lambda^2} \right)^3 \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int D(\xi_1) D(\xi_2) f_T(\mathbf{x}_1, \xi_1, 0) f_T(\mathbf{x}_2, \xi_2, 0)$$

$$\times \left(\int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1) [(\mathbf{x}_1 + \lambda\xi_1(s_1)) \cdot \nabla_r][(\mathbf{x}_2 + \lambda\xi_2(s_2)) \cdot \nabla_r] \left(\frac{1}{r} \right)_{r=1} \right)^2 \tag{3.9}$$

$C(\beta, \rho)$ is negative since $f_T(\mathbf{x}, \xi, 0) \geq 0$ (see (3.5)). This establishes the point (i) of section 1.

The high temperature behaviour of $C(\beta, \rho)$ can be seen directly on formula (3.9). Notice first from (2.18) that $F(\xi) = O(\kappa)$, $\kappa \simeq \sqrt{\beta\rho}$, so

$$e^{-\beta F(\xi)} = 1 + O(\beta^{3/2}\rho) \tag{3.10}$$

Thus for β small, $f_T(\mathbf{r}, \xi, 0)$ (3.5) can be approximated by

$$f_T(\mathbf{r}, \xi, 0) \simeq \beta e^2 \int_0^1 ds V_\kappa(\mathbf{r} + \lambda\xi(s)) \tag{3.11}$$

Hence using (2.16), (3.1) and (3.11) the dominant contribution to the normalization factor A as $\beta \to 0$ is given by

$$A = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \int d\mathbf{r} \int D(\xi) f_T(\mathbf{r}, \xi, 0) \tag{3.12}$$

$$\simeq \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \beta e^2 \int D(\xi) \int d\mathbf{r} \frac{e^{-\kappa r}}{r} \equiv \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \frac{B}{\rho} \tag{3.13}$$

Making the same approximation (3.11) on the numerator of (3.9) leads to

$$C(\beta, \rho) \simeq -\frac{\beta e^4}{2} \lambda^4 \int D(\xi_1) D(\xi_2)$$

$$\times \left(\int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1)[\xi_1(s_1) \cdot \nabla_r][\xi_1(s_2) \cdot \nabla_r] \left(\frac{1}{r}\right)_{r=1}\right)^2 \tag{3.14}$$

But this expression (up to a factor $-\beta$) is exactly that found for the high temperature correlation of two (unbound) charges [5]; it can be calculated with the result stated in point (ii) of section 1 (see sec.VII of [5], formulae (7.26), (7.27) there).

4   The low temperature and low density limit

In order to determine the low temperature limit of $C(\beta, \rho)$ in terms of atomic eigenvalues and eigenstates, one must convert the expression (3.9) back in operator langage. This can be done by applying the Feynman-Kac formula backwards to (3.9). Recalling here that $\rho = e^{-\delta\beta}$ will be exponentially small as $\beta \to \infty$ one can replace $e^{-\beta F(\xi)}$ by 1 in (2.17) (see (3.10))[5]. Then one finds that (3.9) has the equivalent expression

$$C(\beta, \rho) = -\frac{e^4}{2A^2\beta^3} \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta dt_1 \int_0^\beta dt_2 \times$$

$$(\beta\delta(s_1 - s_2) - 1)(\beta\delta(t_1 - t_2) - 1) \sum_{\mu\nu\rho\sigma} d_{\mu\rho} d_{\nu\sigma} K_{\mu\nu}(s_1 - t_1) K_{\rho\sigma}(s_2 - t_2) \tag{4.1}$$

$$d_{\mu\rho} = \partial_\mu \partial_\rho \left(\frac{1}{r}\right)_{r=1}$$

Here $K_{\mu\nu}(s - t)$ are the position-position imaginary time ordered correlations

$$K_{\mu\nu}(s - t) = \text{Tr}\left\{e^{-\beta H} \mathcal{T}(x_\mu(s) x_\nu(t)) - e^{-\beta H_0} \mathcal{T}(x_\mu^0(s) x_\nu^0(t))\right\} \tag{4.2}$$

where $\mathcal{T}$ is the chronological operator, $H = H_0 + V_\kappa$, $H_0 = \frac{|\mathbf{p}^2|}{2m}$, is the hamiltonian of the Debye atom[6] and

$$x_\mu(s) = \exp(sH) x_\mu \exp(-sH), \quad x_\mu^0(s) = \exp(sH_0) x_\mu \exp(-sH_0)$$

---

[5]This exponentially small error on $C(\beta, \rho)$ will not be mentionned any more in the sequel.

[6]The index κ is ommited on H; it is understood that H is the hamiltonian of the screened atom unless stated otherwise.

are imaginary time evolved position operators. These correlations are the operator form of the dipoles occuring in (3.9). The substraction of the freely evolving quantities (originating from the truncations) insures the finiteness of the trace.

It is expected that the dominant low temperature terms will come from the ground state contribution of $\exp(-\beta H)$ when evaluating the trace. Let P be the projection on the ground state of H, $Q = I - P$, and decompose $U(s) = \exp(-sH) = U_P(s) + U_Q(s)$ accordingly. We split

$$K_{\mu\nu}(s - t) = K_{\mu\nu}^{(1)}(s - t) + K_{\mu\nu}^{(2)}(s - t) \tag{4.3}$$

The first term $K_{\mu\nu}^{(1)}(s - t)$ is the part that has at least one ground state contribution (writing also the time ordering explicitly)

$$\begin{aligned}
K_{\mu\nu}^{(1)}(s - t) \;=\; & \theta(s - t)\{\operatorname{Tr} U_P(\beta - s + t)x_\mu U_P(s - t)x_\nu \\
& + \; \operatorname{Tr} U_P(\beta - s + t)x_\mu U_Q(s - t)x_\nu \\
& + \; \operatorname{Tr} U_Q(\beta - s + t)x_\mu U_P(s - t)x_\nu\} \\
& + \; \text{same expression with } (s,t) \text{ and } (\mu,\nu) \text{ permuted}
\end{aligned} \tag{4.4}$$

Since P is one dimensional, traces are well defined in (4.4). It is shown in the appendix that the remaining part $K_{\mu\nu}^{(2)}(s - t)$, which contains ionized states of both atoms, does not contribute to the low temperature limit. To analyse $K_{\mu\nu}^{(1)}(s - t)$ further, we introduce the spectral representation

$$e^{-sH} = \int e^{-s\varepsilon} F(d\varepsilon) \tag{4.5}$$

where $F(\varepsilon)$ is the spectral family of H. Then (4.4) reads

$$\begin{aligned}
K_{\mu\nu}^{(1)}(s - t) \;=\; & \theta(s - t) \int d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) e^{-(\beta - s + t)\varepsilon_1} e^{-(s-t)\varepsilon_2} \\
& + \; \theta(t - s) \int d\Sigma_{\nu\mu}(\varepsilon_1, \varepsilon_2) e^{-(\beta - t + s)\varepsilon_1} e^{-(t-s)\varepsilon_2}
\end{aligned} \tag{4.6}$$

We have defined the joint measure on the product of the energy spectra

$$\begin{aligned}
d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) \;=\; & \operatorname{Tr} F_P(d\varepsilon_1)x_\mu F_P(d\varepsilon_2)x_\nu \\
& + \; \operatorname{Tr} F_P(d\varepsilon_1)x_\mu F_Q(d\varepsilon_2)x_\nu + \operatorname{Tr} F_Q(d\varepsilon_1)x_\mu F_P(d\varepsilon_2)x_\nu
\end{aligned} \tag{4.7}$$

Since $F_P(E_0) = P$ is the projection on the ground state ψ_0 of H, one can write more explicitly

$$d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) = \delta(\varepsilon_1 - E_0)\delta(\varepsilon_2 - E_0)(\psi_0, x_\mu\psi_0)(\psi_0, x_\nu\psi_0)d\varepsilon_1 d\varepsilon_2$$

$$+ \; \delta(\varepsilon_1 - E_0)(x_\mu\psi_0, F_Q(d\varepsilon_2)x_\nu\psi_0)d\varepsilon_1 + \delta(\varepsilon_2 - E_0)(x_\nu\psi_0, F_Q(d\varepsilon_1)x_\mu\psi_0)d\varepsilon_2 \tag{4.8}$$

with the obvious symmetry

$$d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) = d\Sigma_{\nu\mu}(\varepsilon_2, \varepsilon_1) \tag{4.9}$$

When (4.3) and (4.6) are inserted in (4.1) one obtains

$$C(\beta, \rho) = -\frac{e^4}{2A^2\beta^3} \sum_{\mu\nu\rho\sigma} d_{\mu\rho} d_{\nu\sigma}$$

$$\times \int d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) \int d\Sigma_{\rho\sigma}(\varepsilon_3, \varepsilon_4) I_\beta(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4) + R(\beta, \rho) \tag{4.10}$$

where $I_\beta(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4)$ is the multiple time integral

$$I_\beta(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4) = \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta dt_1 \int_0^\beta dt_2 \left((\beta\delta(s_1 - s_2) - 1)(\beta\delta(t_1 - t_2) - 1) \right)$$

$$\times \quad e^{(s_1 - t_1)(\varepsilon_1 - \varepsilon_2)} \{\theta(s_1 - t_1)e^{-\beta\varepsilon_1} + \theta(t_1 - s_1)e^{-\beta\varepsilon_2}\}$$
$$\times \quad e^{(s_2 - t_2)(\varepsilon_3 - \varepsilon_4)} \{\theta(s_2 - t_2)e^{-\beta\varepsilon_3} + \theta(t_2 - s_2)e^{-\beta\varepsilon_4}\} \tag{4.11}$$

and the remainder $R(\beta, \rho)$ includes the contributions of $K^{(2)}$. To obtain (4.10) and (4.11) we have used (4.9) to regroup the two terms in (4.6). The integral (4.11) can be calculated with the result

$$I_\beta(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4) = \beta^3 \frac{e^{-\beta(\varepsilon_2 + \varepsilon_4)} - e^{-\beta(\varepsilon_1 + \varepsilon_3)}}{\varepsilon_1 + \varepsilon_3 - \varepsilon_2 - \varepsilon_4}$$
$$+ \beta^2 \frac{e^{-\beta(\varepsilon_1 + \varepsilon_4)} + e^{-\beta(\varepsilon_2 + \varepsilon_3)} - e^{-\beta(\varepsilon_1 + \varepsilon_3)} - e^{-\beta(\varepsilon_2 + \varepsilon_4)}}{(\varepsilon_1 - \varepsilon_2)(\varepsilon_3 - \varepsilon_4)} \tag{4.12}$$

Note that $I_\beta(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4) = 0$ if $\varepsilon_1 = \varepsilon_2$ or (and) $\varepsilon_3 = \varepsilon_4$ (as seen directly on (4.11)). We can therefore consider, when calculating the integral (4.10), that the measure has no support at $\varepsilon_1 = \varepsilon_2$ and $\varepsilon_3 = \varepsilon_4$. Inserting (4.12) in (4.10) and using again the symmetry (4.9) leads to

$$C(\beta, \rho) = \frac{e^4}{A^2} \sum_{\mu\nu\rho\sigma} d_{\mu\rho} d_{\nu\sigma} \int d\Sigma_{\mu\nu}(\varepsilon_1, \varepsilon_2) d\Sigma_{\rho\sigma}(\varepsilon_3, \varepsilon_4)$$

$$\times \left[\frac{e^{-\beta(\varepsilon_1 + \varepsilon_3)}}{\varepsilon_1 + \varepsilon_3 - \varepsilon_2 - \varepsilon_4} + \frac{1}{\beta} \frac{e^{-\beta(\varepsilon_1 + \varepsilon_4)} - e^{-\beta(\varepsilon_2 + \varepsilon_3)}}{(\varepsilon_1 - \varepsilon_2)(\varepsilon_3 - \varepsilon_4)} \right] + R(\beta, \rho) \tag{4.13}$$

We are now in position to take the low temperature limit. The dominant contribution comes from the first term in the integrand when $\varepsilon_1 = \varepsilon_3 = E_0$ (i.e. from the second term of the measure (4.8)). The other one is exponentially smaller since then both ε_2 and ε_4 must be larger or equal to the first excited atomic state. Moreover all spectral quantities of the Debye atom converge to those of the hydrogen atom as $\kappa \to 0$ ($V - V_\kappa$ is a bounded perturbation of the Coulomb potential with $\|V - V_\kappa\| = O(\kappa)$). For the normalization factor, we have from (3.12) and the Feynman-Kac formula (see also the appendix, lemma 3)

$$A = \text{Tr} \left(e^{-\beta H} - e^{-\beta H_0} \right) \simeq e^{-\beta E_0}, \quad \beta \to \infty \tag{4.14}$$

Combining these facts with the result (.11) of the appendix on $R(\beta, \rho)$ yields with $\rho = e^{-\delta\beta}$

$$\lim_{\beta \to \infty} C(\beta, \rho) = e^4 \sum_{\mu\nu\rho\sigma} d_{\mu\rho} d_{\nu\sigma}$$

$$\times \int \int \frac{(x_\mu \psi_0, F_Q(d\varepsilon_2) x_\nu \psi_0)(x_\rho \psi_0, F_Q(d\varepsilon_4) x_\sigma \psi_0)}{2E_0 - \varepsilon_2 - \varepsilon_4} \tag{4.15}$$

where now all quantities belong to the hydrogen atom. But this is identical to the van der Waals coefficient (1.4) and proves the point (iii) of section 1.

5   Concluding remarks

We have shown in this model that the usual van der Waals potential appears naturally in the atomic limit as the r^{-6}-correlation tail that exists generally between quantum charges. In this limit, the amplitude of this interaction is exponentially close to the van der Waals coefficient C_w. In fact, as seen from (4.13), both quantities differ by an error $O(\exp(-(E_1 - E_0)/k_B T))$ where E_1 is the first excited state of the atom[7]. On the other hand, this amplitude vanishes as T^{-3} as $T \to \infty$. One can conjecture that these behaviours will remain the same in the full electron-proton gas. Here the problem can be conveniently studied with the diagrammatic techniques developped in [6] and this will be the subject of a future work.

Acknowledgements

Appendix

Lemma 1 Assume that $H = H_0 + V$, $H_0 = -\frac{1}{2}\Delta$, $V \in \mathcal{L}^2 + \mathcal{L}^\infty$, has a ground state ψ_0 with energy E_0 ($E_0 < 0$). Let P be the spectral projection on ψ_0, $Q = I - P$, and $E_1 = \mathrm{infspec}(HQ)$. Then for ε sufficiently small

$$e^{-sH}Q \leq e^{-s(E_1 + o(\varepsilon))}Q e^{-\beta \varepsilon H_0}Q, \quad s \geq 0 \tag{.1}$$

Proof :

Write

$$
\begin{aligned}
HQ &= Q((1 - \varepsilon)H_0 + V)Q + \varepsilon Q H_0 Q \\
&= (1 - \varepsilon)Q(H + \lambda V)Q + \varepsilon Q H_0 Q, \quad \lambda = \frac{\varepsilon}{1 - \varepsilon}
\end{aligned} \tag{.2}
$$

If $\varphi \in \mathcal{D}(H) = \mathcal{D}(H_0)$, one has

$$-2\|H_0\psi_0\|(\varphi, \varphi) \leq (\varphi, (PH_0 + H_0P)\varphi) \leq 2\|H_0\psi_0\|(\varphi, \varphi)$$

and hence, since H_0 is positive,

$$QH_0Q = H_0 - PH_0 - H_0P + PH_0P \geq H_0 - 2\|H_0\psi_0\| \tag{.3}$$

---

[7]The estimation of $R(\beta, \rho)$ can be improved to $O(\exp(-(E_1 - E_0)/k_B T))$ if one chooses P to be the projection on a finite set of excited states. We have taken P equal to the ground state projection for the simplicity of the presentation.

If λ is small enough, $H + \lambda V$ has a ground state energy $E_{0,\lambda}$ with projection P_λ. Then with $Q_\lambda = I - P_\lambda$

$$
\begin{aligned}
Q(H + \lambda V)Q &= Q_\lambda(H + \lambda V)Q_\lambda \\
&+ (P - P_\lambda)(H + \lambda V)Q_\lambda + Q(H + \lambda V)(P_\lambda - P)
\end{aligned} \tag{.4}
$$

By regular perturbation theory,

$$
(H + \lambda V)(P_\lambda - P) = (E_0 - E_{0,\lambda})P + E_{0,\lambda}(P - P_\lambda) - \lambda(H_0 - E_0)P
$$

tends to zero in norm as $\lambda \to 0$. Hence

$$
Q(H + \lambda V)Q \geq \mathrm{infspec}(Q_\lambda(H + \lambda V)Q_\lambda) + o(\lambda) = E_1 + o(\lambda) \tag{.5}
$$

Both inequalities (.3) and (.5) hold as forms on $\mathcal{D}(H_0)$. Combining them in (.2) yields

$$
HQ \geq \varepsilon H_0 + E_1 + o(\varepsilon)
$$

and this leads to (.1).

Lemma 2 Let $\| \cdots \|_2$ be the Hilbert-Schmidt norm, then

$$
\|e^{-sH_0}V\|_2 \leq \frac{C}{s^{3/4}}\|V\|_{\mathcal{L}^2} \tag{.6}
$$

Proof : By direct calculation with the free kernel $(2\pi s)^{-3/2} \exp\left(-\frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{2s}\right)$.

Lemma 3 Let H be the hamiltonian of the Debye atom and fix ε as in lemma 1. Then for β large and ρ small

$$
\mathrm{Tr}\left(e^{-\beta H} - e^{-\beta H_0}\right) = e^{-\beta E_0} + O\left(\frac{e^{-\beta(E_1 + o(\varepsilon))}}{\rho}\right) \tag{.7}
$$

Lemma 4 Let U_Q as in section 4, $U^0(s) = e^{-sH_0}$ and

$$
h_{\mu\nu}(s) = \mathrm{Tr}\left(U_Q(\beta - s)x_\mu U_Q(s)x_\nu - U^0(\beta - s)x_\mu U^0(s)x_\nu\right) \tag{.8}
$$

Then for β large and ρ small

$$
h_{\mu\nu}(s) \leq C\frac{\beta^\alpha e^{-\beta(E_1 + o(\varepsilon))}}{\rho^\eta}, \quad \alpha, \eta > 0, \tag{.9}
$$

Here and in the sequel, C is a generic constant (that depends in general on ε). The rest $R(\beta, \rho)$ in (4.10) involving the continuous spectra of both atoms can now easily be estimated. $R(\beta, \rho)$ is given by the expression (4.1) with $K_{\mu\nu}K_{\rho\sigma}$ replaced by $K_{\mu\nu}^{(1)}K_{\rho\sigma}^{(2)} + K_{\mu\nu}^{(2)}K_{\rho\sigma}^{(1)} + K_{\mu\nu}^{(2)}K_{\rho\sigma}^{(2)}$ and

$$
K_{\mu\nu}^{(2)}(s - t) = \theta(s - t)h_{\mu\nu}(s - t) + \theta(t - s)h_{\nu\mu}(t - s)
$$

From the estimate (.9) all the time integrals in (4.1) give atmost powers of β. Hence, noting also that $K_{\mu\nu}^{(1)}(s) = O(e^{-\beta E_0})$, one has

$$|R(\beta, \rho)| \leq C \frac{\beta^\alpha e^{-\beta(E_0 + E_1 + o(\varepsilon))}}{A^2 \rho^\eta} \tag{.10}$$

Set $\rho = e^{-\delta\beta}$, $\delta > 0$, β large. Then we can identify E_0 and E_1 to the ground state and first excited state of the hydrogen atom up to a vanishingly small error as $\beta \to \infty$. Choosing

$$\delta < \min\{1, \eta^{-1}\}(E_1 - E_0 + o(\varepsilon))$$

it follows from lemma 3 that $A = \text{Tr}\left(e^{-\beta H} - e^{-\beta H_0}\right) \simeq e^{-\beta E_0}$ and therefore

$$|R(\beta, \rho)| \leq C\beta^\alpha e^{-\beta(E_1 - E_0 + o(\varepsilon) - \delta\eta)} \tag{.11}$$

tends to zero exponentially fast as $\beta \to \infty$.

Proof of lemma 3

$$\text{Tr}\left(e^{-\beta H} - e^{-\beta H_0}\right) = e^{-\beta E_0} + \text{Tr}\, Q(e^{-\beta H} - e^{-\beta H_0})Q - \text{Tr}\, e^{-\beta H_0}P \tag{.12}$$

If $\|\cdots\|_1$ is the trace norm

$$
\begin{aligned}
\text{Tr}\, Q(e^{-\beta H} - e^{-\beta H_0})Q &\leq \int_0^\beta dt \|Q e^{-(\beta-t)H} V e^{-t H_0} Q\|_1 \\
&\leq \int_0^\beta f(\beta - t) g(t)
\end{aligned}
\tag{.13}
$$

with

$$f(s) = \|Q e^{-sH} |V|^{1/2}\|_2, \quad g(t) = \||V|^{1/2} e^{-t H_0} Q\|_2$$

It follows from lemmas 1 and 2 that

$$
\begin{aligned}
f(s) &= \left(\text{Tr}\, |V|^{1/2} Q e^{-2sH} |V|^{1/2}\right)^{1/2} \\
&\leq e^{-s(E_1 + o(\varepsilon))} \left(\text{Tr}\, |V|^{1/2} Q e^{-2\varepsilon s H_0} Q |V|^{1/2}\right)^{1/2} \\
&\leq e^{-s(E_1 + o(\varepsilon))} \|e^{-\varepsilon s H_0} Q |V|^{1/2}\|_2 \\
&\leq e^{-s(E_1 + o(\varepsilon))} \left[\|e^{-\varepsilon s H_0} |V|^{1/2}\|_2 + \|e^{-\varepsilon s H_0} P |V|^{1/2}\|_2\right] \\
&\leq e^{-s(E_1 + o(\varepsilon))} \left[\frac{C}{s^{3/4}} \||V|^{1/2}\|_{\mathcal{L}^2} + \||V|^{1/2}\psi_0\|\right]
\end{aligned}
\tag{.14}
$$

By scaling,

$$\||V|^{1/2}\|_{\mathcal{L}^2} = \left(\int d\mathbf{r} \frac{e^{-\kappa r}}{r}\right)^{1/2} = O(\kappa^{-1}) \tag{.15}$$

and $\||V|^{1/2}\psi_0\|$ remains bounded as $\kappa \to 0$, hence with $\kappa \simeq (\beta\rho)^{1/2}$

$$f(s) \leq C \frac{e^{-s(E_1 + o(\varepsilon))}}{\rho^{1/2} s^{3/4}}, \quad \beta \to \infty, \ \rho \to 0 \tag{.16}$$

and the same estimate holds for $g(t)$. When these estimates are inserted in (.13) one obtains

$$\operatorname{Tr} Q(e^{-\beta H} - e^{-\beta H_0})Q = O\left(\frac{e^{-\beta(E_1 + o(\varepsilon))}}{\rho}\right), \quad \beta \to \infty, \quad \rho \to 0$$

and since $\operatorname{Tr} e^{-\beta H_0}P \le 1$, this proves the lemma 3.

Proof of lemma 4

We replace first U^0 by $U_Q^0 = QU^0Q$ in (.8) and write

$$\operatorname{Tr}\left(U_Q(\beta - s)x_\mu U_Q(s)x_\nu - U_Q^0(\beta - s)x_\mu U_Q^0(s)x_\nu\right) = J_1 + J_2 + J_3$$

$$
\begin{aligned}
J_1 &= \operatorname{Tr}\left(U_Q(\beta - s) - U_Q^0(\beta - s)\right)x_\mu(U_Q(s) - U_Q^0(s))x_\nu \\
J_2 &= \operatorname{Tr}\left(U_Q(\beta - s) - U_Q^0(\beta - s)\right)x_\mu U_Q^0(s)x_\nu \\
J_3 &= \operatorname{Tr} U_Q^0(\beta - s)x_\mu(U_Q(s) - U_Q^0(s))x_\nu
\end{aligned}
\tag{.17}
$$

and

$$J_1 \le \|(U_Q(\beta - s) - U_Q^0(\beta - s))x_\mu\|_2 \|(U_Q(s) - U_Q^0(s))x_\nu\|_2 \tag{.18}$$

These factors are treated as in (.13) with the difference that $g(t)$ is estimated here by the operator norm

$$\|(U_Q(s) - U_Q^0(s))x_\mu\|_2 \le \int_0^s dt\, f(s - t)g(t) \tag{.19}$$

with

$$
\begin{aligned}
g(t) &= \||V|^{1/2}e^{-tH_0}Qx_\mu\| \le \||V|^{1/2}e^{-tH_0}x_\mu\| + \||V|^{1/2}e^{-tH_0}Px_\mu\| \\
&\le \||V|^{1/2}x_\mu e^{-tH_0}\| + \||V|^{1/2}tp_\mu e^{-tH_0}\| + \||V|^{1/2}e^{-tH_0}Px_\mu\| \\
&= A_1 + \dot{A}_2 + A_3
\end{aligned}
\tag{.20}
$$

where we have used the relation

$$[e^{-tH_0}, x_\mu] = -itp_\mu e^{-tH_0} \tag{.21}$$

Now

$$A_1 \le \||V|^{1/2}x_\mu\| \le \sup_r\left(\exp(-\frac{\kappa r}{2})\sqrt{r}\right) = O\left(\frac{1}{\sqrt{\kappa}}\right) \tag{.22}$$

Lemma 2 and (.15) imply

$$A_2 \le \||V|^{1/2}e^{-\frac{1}{2}tH_0}\|_2 \|tp_\mu e^{-\frac{1}{2}tH_0}\| \le \frac{C}{t^{1/4}}\||V|^{1/2}\|_{\mathcal{L}^2} = O\left(\frac{1}{\kappa t^{1/4}}\right) \tag{.23}$$

since $\|\sqrt{t}p_\mu e^{-\frac{1}{2}tH_0}\|$ is bounded with respect to t. Finally

$$A_3 \le \||V|^{1/2}e^{-tH_0}\psi_0\| \|x_\mu\psi_0\|$$

$$\leq \||V|^{1/2}(H_0 + I)^{-1}\|_2\|e^{-tH_0}(H_0 + I)\psi_0\|\|x_\mu\psi_0\| \leq C\||V|^{1/2}\|_{\mathcal{L}^2} = O(\kappa^{-1}) \qquad (.24)$$

Collecting these results gives $(\kappa \simeq (\beta\rho)^{1/2})$

$$g(t) \leq C\frac{1}{\rho^{1/2}t^{1/4}}, \quad \beta \to \infty, \quad \rho \to 0 \qquad (.25)$$

Inserting (.16) and (.25) in (.19) yields

$$\|(U_Q(s) - U_Q^0(s))x_\mu\|_2 \leq C\frac{e^{-s(E_1 + o(\varepsilon))}}{\rho}$$

showing that J_1 verifies an estimate of the form (.7). We let the reader convince himself by similar methods that the same is true for J_2 and J_3[8]. The quantities (.17) still differ from $h_{\mu\nu}(s)$ (.8) by

$$\mathrm{Tr}\left(U^0(\beta - s)x_\mu U^0(s)x_\nu - U_Q^0(\beta - s)x_\mu U_Q^0(s)x_\nu\right)$$

but the latter contribution is a sum of terms involving at least a ground state projection P and only free evolutions. It is easy to check, using (.21), that they can atmost grow as powers of β and this concludes the proof of the lemma 4.

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[8]The analysis shows that one can take $\eta = 5/4$ in (.9).