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Correlation effects in a few-particle one-dimensional Coulomb-interacting system

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Summary. A model of the one-dimensional Coulomb-interacting few-particle system is studied in detail. The model is similar to a many-electron system which in a zero-order approximation of the non-interacting particles has only singly occupied one-electron levels. Such model cancels the divergencies in the Coulomb and exchange interaction energies found regularly for a conventional one-dimensional system which is built up of the doubly occupied one-electron levels and is submitted to the Coulomb perturbation. In the present case, the correlated wave functions for the system can be obtained from the Slater determinants constructed for the sets of the one-electron levels and combined according to the rules given by the standard perturbation theory.

The calculations allow us to discuss the correlation influence and the effect of the size of the model on: (i) the excitation energies including the criterion corresponding to the metal–insulator transition (the Mott transition), (ii) the distribution of the correlated charge along the model, (iii) the average velocity of a two-particle system being in different states, and (iv) the dipole moments and transition probabilities. In the last case, the lifetime of the uncorrelated and correlated excited states obtained in the situation of the allowed one-photon transitions can be compared with the lifetime obtained for a similar system in the case when the one-photon transitions are forbidden and two-photon transitions should be taken into account.

No data other than the length of the model and the fundamental constants of nature enter the calculations.

Key words: One-dimensional model – Coulomb-correlated excitation energies – Coulomb-correlated particle density – Mott transitions – Dipole transition probabilities

1 Introduction

The one-dimensional many-electron problem has its rich literature; see e.g. [1–21]. In many cases these investigations seemed to be rather academic because of the absence of their experimental counterparts. Historically, the sound-waves-like approach to the many-electron problem by Tomonaga, which was similar to

Bohm's idea of the plasma oscillations in the electron gas, seemed to be the first one-dimensional electron–electron interaction theory [22–27]. Then came the spectroscopy of molecules having the conjugated double-bond systems for which also the free-electron model appeared suitable [28–36]. In the next step, the problem found its stimulus in the Little's prediction [37] of high-temperature superconductivity in the one-dimensional systems having the branched chains; cf. here also [38–44]. After that there came the effects of high conductivity in some long polymers (TTF-TCNQ compounds) which could be approximately considered as the one-dimensional systems [45–56]. Recently, however, the electronic structure of quasi one-dimensional systems as realized in quasi one-dimensional quantum wires is under the experimental study [57, 58]. Also the one-dimensional quantum wells have been recently considered both experimentally and theoretically [59, 60]. This was possible with the increasing microelectronic fabrication techniques which enabled us to study a wide range of the physical phenomena concerning the electronic structures having the reduced dimensionality and a rather small electron number. These phenomena attracted much of interest in the past few years; see e.g. [61, 62]. The best known are probably the quantum Hall effect and the behavior of the low-dimensional systems in strong magnetic fields [63–66]. At the same time the accurate calculations of the many-body effects in the one-dimensional systems were lacking. This lack was most probably due to the divergencies which necessarily occur in the energy calculations done for the electron–electron interaction in the one-dimensional systems. Similar calculations for any three-dimensional many-electron case are normally convergent. Nevertheless, with some allowances imposed on the parameters characteristic for the one-dimensional models, the electron–electron interaction calculations could be performed too, and, in particular, an important role of the exchange interactions in the one-dimensional systems was exhibited [61, 62].

The well-known idealization of a one-dimensional electron gas with Coulomb interactions is provided by the Luttinger model [67–69]. When generalized to describe spin-$\frac{1}{2}$ fermions the model is exactly soluble [68, 69]; it can be diagonalized in terms of a set of exact boson modes describing charge and spin-density waves [10, 70, 71]. The model can be completed by including the "backward scattering" ($2\ k_F$ momentum transfer) processes in which particles on opposite sites of the Fermi surface can be exchanged [72]. A feature of such solution is that an exact decoupling of charge and spin degrees of freedom can occur. A mapping of the spin part of this "backward scattering" model was reported in [73]. The defects of the "backward scattering" model were pointed out in [74, 75], where in fact the lowest-order interactions between charge and spin density waves in a generalized model are obtained which included the "backward scattering" and did not need the cut-off parameter introduced in [10]; see also [76, 77]. The main idea was that the parameter limit is not required if a properly normal-order boson representation is constructed.

The properties of organic metals and other highly conducting solids are far too complex to be understood by means of purely microscopic calculations. Usually it is assumed that the restriction to one-dimensional motion improves possibility of finding exact solutions of certain many-body problems [78]. In real materials there are strong Coulomb repulsive forces, but it seems to be necessary to consider also the attractive potentials because they may well arise when electrons delocalize on large molecules (thereby reducing the Coulomb force) and attractive couplings are induced by molecular polarizability, or other collective effects [78, 37–43].

Solyom [79] gave a review of the theoretical approach to the one-dimensional conductors. Especially, he discussed the exact solutions known for particular values of the coupling constants in a single one-dimensional system (Tomonaga–Luttinger model, Luther–Emery model [72]). Tomonaga simplified considerably the problem of the one-dimensional electron system with a long-range interaction by linearizing the energy dispersion around the two Fermi points $\pm k_F$. On the next step, the Luttinger model assumed an exactly linear dispersion. The both models show the same low-energy physics for long-range interaction with a rather weak restriction on the interaction strength [25, 80]. Also the one-dimensional Hubbard model, which is exactly solvable by the Bethe ansatz method [81], is similar to a Luttinger liquid for any coupling strength except for half-filling [82, 83]. In [72] it was realized, using the bosonized Hamiltonian, that for particular values of the couplings the backward scattering problem can again be solved exactly. Electron–electron scattering and the transport relaxation time coming from that scattering were calculated in that region of temperatures where the kinetic equation can be used [84]. Moreover, it was demonstrated that the interaction between electrons can give rise to an essential temperature dependence of the conductivity [79, 85].

Recently, high-resolution photoemission experiments were carried out [86] on one-dimensional organic conductors which exhibit an intriguing spectroscopic behavior; see also [87, 88] : in contrast to usual metals, the spectral function vanishes at the Fermi level and no Fermi edge is detectable. The peculiarities of correlated electrons in one dimension were examined theoretically in this context on the basis of the Tomonaga–Luttinger model [82, 89]. Other theoretical approaches to the one-dimensional systems rely on the exactly solvable one-dimensional $1/r$-Hubbard model. Recently, it was found out that no kind of the wave functions obtained for this model (Hartree–Fock, Gutzwiller, Baeriswyl and combined Gutzwiller–Baeriswyl wave functions) can correctly reproduce the physics of the metal-to-insulator transition which occurs in this model [90]. Other, rather recent, calculations on the Hubbard-like model and its cousin, the $t - J$ model, are given in [91, 92]. Recent papers on the one-dimensional models directed towards their application to the molecular systems are [93–98].

In the present paper our point is that we can find and apply the model in which all conventional interactions in the electron gas, viz. the Coulomb, exchange and those responsible for the high-order correlation effects, can remain convergent also in the case when the model becomes strictly one-dimensional, i.e. when the cross-section radius R of the quantum-well wire tends to zero. This allows us for a considerable simplification of the calculations and, at the same time, enables one for the theoretical treatment of the effects which usually escaped from a careful examination. We assume our model is Coulomb interacting with half-filled spin-independent electron levels. Hence, it is within the perturbatively controlled regime; recently the validity of this regime for the electron gas was discussed by Anderson [99]. The first of the many-body effects which can be put under consideration are the well-known problems of the electron excitation and the hole creation in the Fermi few-particle system. We may ask, in the first step, how the electron correlation influences the excitation energy in dependence on the electron level position in the energy spectrum of that system and the size of the one-electron excitation energy itself. In the next step a question may arise, and can be solved, how the electron correlations influence the lifetime of the excited electron–hole pair. In this case the lifetime of two-photon transitions between dipole-forbidden levels can also be examined. This can be done for different states taken as the intermediate states and a different size of the parameter characterizing the sample of the one-dimensional system which has its length L. Special conditions for the occurrence of the Mott transition in the correlated one-dimensional system are also investigated. This last point requires some explanation. In case of an uncorrelated electron gas we have an almost exactly uniform distribution of the electron charge along the length of the potential cylindrical well (potential box). At $R \to 0$ this distribution leads usually to an infinite interaction energy of the gas enclosed in the potential well already in the first-order approximation of the perturbation theory. On the other hand, in the present model of the gas, we have a finite electron–electron interaction energy also at $R \to 0$ at any order of the perturbation theory. Apart from the radius R there exist also two other parameters characterizing the gas model: the box length L and the electron number N. In the Mott transition we have a rapid change of the density distributed in a roughly discrete way about the individual atoms into a quasi-uniform density distribution extended throughout the volume of the crystal block. Our purpose is to examine to what extent the pattern of electron excitations characteristic for a metal can be changed, due to the electron correlation, into a pattern characteristic for an insulator, and how this change can depend on the model parameters L and N.

Usually the answer of the questions stated above requires the application of a complicated many-body technique. In the present model the questions concerning the one-dimensional gas model can be approached in an almost analytic way developed on the basis of the conventional perturbation theory.

2 The model

The model applied in this paper is based on the assumption that all particle levels in the Coulomb-interacting gas can be only singly occupied. For example, the particles can be electrons having only one kind of spin. This means we exclude any double occupancy of the electron space orbitals. In effect, any unperturbed electron wave function of the gas can be represented by a single Slater determinant irrespective of the fact whether all one-electron levels of the gas are successively occupied beginning from the lowest occupied level (in this case we have a ground state of the gas), or there exist some, one or more, gaps in the occupation sequence of the levels (then we say the gas is in its excited state). The energy of any of such occupation patterns can be calculated in the zero-order approximation (the non-interacting, or the Fermi, energy of the system), then in the first-order approximation (the first order, or the Hartree–Fock energy of the system), and finally, the interaction energy of any pattern can be calculated in the second, the third and the further orders of the Rayleigh–Schrödinger (RS) perturbation theory leading to the successive approximations of the correlation energy of the system. Any correlation energy calculated in such a way is dependent on a given occupation pattern of the one-electron levels. To the best of our knowledge such kind of the calculations have never been performed before for a free-particle one-dimensional system composed of a finite number of particles. In the case where the system was a three-dimensional one and the particles were free electrons for which the spin degeneracy was allowed for, the correlation energy was approached in a former paper on the basis of the RS perturbation theory [100].

The main purpose of our simplifying assumption concerning the gas model presented at the beginning of this section was to avoid divergencies in the calculations of the electron interaction energy when $R \to 0$. But the assumption that

$R \to 0$ enables us also to calculate the matrix elements entering the perturbation formalism in a very simple form.

The one-electron (zero-order) energy of the system of N electrons is a sum of one-electron eigenenergies which give

$$E^{(0)} = \frac{\hbar^2}{2m_e} \sum_k \frac{k^2\pi^2}{L^2} + \frac{\hbar^2}{2m_e} \sum_k u_{01}^2 = \frac{\hbar^2}{2m_e} \sum_k \frac{k^2\pi^2}{L^2} + N \frac{\hbar^2}{2m_e} u_{01}^2; \tag{1}$$

the first sum in Eq. (1) represents the kinetic energy of the motion along the potential box having the length L, the second sum represents the kinetic energy of the motion transversal to L. The potential box has a cylindrical shape of radius R and infinite walls, so the one-electron wave functions can be represented in a standing-like form; see [101–105] and Eq. (3) below. The k in the sum runs over all occupied one-electron levels. The number

$$u_{01} = 2.405\,(R^{-1}) \tag{2}$$

is the first zero of the Bessel function J_0 entering the radial part of the one-electron wave function which diagonalizes the kinetic energy operator:

$$\varphi_k(r) = \left(\frac{2}{L}\right)^{1/2} N_{01} J_0(u_{01} r) \sin(k\pi z/L); \tag{3}$$

$[N_{01} = 2.724(2\pi)^{-1/2} R^{-1}]$. For a very small R the number u_{01} can become so large that any excitation energy of the electron system coming from the change of k is smaller than the energy change

$$\frac{\hbar^2}{2m_e}(u_{02}^2 - u_{01}^2) \tag{4}$$

coming from the one-electron excitation from the state represented by the first zero u_{01} of the Bessel function J_0 in Eq. (3) to the state represented by the next zero u_{02} of the same function. In this situation all radial (and angular-dependent) parts of the free-electron wave functions other than those given in Eq. (3) can be neglected as leading to higher one-electron energies than those associated with the change of k. Hence, for all practical calculations of the excitation energies, we have the last term in Eq. (1) unchanged. Evidently, this term cancels in any calculation of the difference of two $E^{(0)}$ representing two patterns of the occupied one-electron levels, giving an expression dependent solely on k's.

The first-order perturbation energy is represented by

$$E^{(1)} = \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}), \tag{5}$$

where

$$J_{ij} = \left\langle ij \left| \frac{e^2}{r_{12}} \right| ij \right\rangle, \tag{6}$$

$$K_{ij} = \left\langle ji \left| \frac{e^2}{r_{12}} \right| ij \right\rangle \tag{7}$$

are, respectively, the conventional Coulomb and exchange integrals. The matrix elements present in Eqs. (6) and (7) are calculated according to the definition

$$\left\langle ab \left| \frac{e^2}{r_{12}} \right| cd \right\rangle = \int \varphi_a^*(\boldsymbol{r}_1)\varphi_b^*(\boldsymbol{r}_2)\frac{e^2}{r_{12}}\,\varphi_c(\boldsymbol{r}_1)\varphi_d(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 \tag{8}$$

suitable for any one-electron levels a, b, c, d. The double sum in Eq. (5) runs over all occupied levels of a given pattern of levels. Any of the integrals (6) and (7) calculated separately for any pair of the levels i and j diverges, but any component of the sum given in Eq. (5), viz., $J_{ij} - K_{ij}$, converges [106]. This leads to a convergent Hartree-Fock energy of the gas. In the next step we have the second-order perturbation energy

$$\sum_{\lambda \neq \nu} \frac{|U_{\nu\lambda}|^2}{E_\nu^{(0)} - E_\lambda^{(0)}}, \tag{9}$$

where $U_{\nu\lambda}$ is the matrix element of the Coulomb interaction between the Slater determinant representing the initial state ν and the Slater determinant representing state λ. For any $\lambda \neq \nu$ the matrix element

$$U_{\nu\lambda} = \frac{1}{2}\sum_i \sum_{j \neq i} \left\langle \Phi_\nu \left| \frac{e^2}{r_{ij}} \right| \Phi_\lambda \right\rangle \tag{10}$$

does not vanish on condition that the Slater determinant Φ_ν differs from a similar Slater determinant Φ_λ only in the occupation of one or two one-electron levels [107]. In the first case, which is a one-electron excitation, let us assume that an electron which is in an occupied level a in the state Φ_ν is promoted to an unoccupied level b creating some new state Φ_λ. Then

$$U_{\nu\lambda} = \sum_c \left[\left\langle ac \left| \frac{e^2}{r_{12}} \right| bc \right\rangle - \left\langle ac \left| \frac{e^2}{r_{12}} \right| cb \right\rangle \right], \tag{11}$$

where the sum runs over all levels c which are occupied in *both* Φ_ν and Φ_λ, so that $c \neq a$ and $c \neq b$. On the next step, in the case when two electrons occupying originally the levels a, b in Φ_ν are shifted to the originally empty levels c, d creating a new state Φ_λ, which leads to a two-electron excitation, we have

$$U_{\nu\lambda} = \left\langle ab \left| \frac{e^2}{r_{12}} \right| cd \right\rangle - \left\langle ab \left| \frac{e^2}{r_{12}} \right| dc \right\rangle. \tag{12}$$

We find that, similar to $J_{ij} - K_{ij}$, expressions (11) and (12) converge also in the case of $R \to 0$. For, we find that

$$\begin{aligned} &\left\langle ab \left| \frac{e^2}{r_{12}} \right| cd \right\rangle - \left\langle ab \left| \frac{e^2}{r_{12}} \right| dc \right\rangle \\ &= I_{|a-c|,|b-d|} - I_{|a-c|,b+d} - I_{a+c,|b-d|} + I_{a+c,b+d} \\ &\quad - I_{|b-c|,|a-d|} + I_{|b-c|,a+d} + I_{b+c,|a-d|} - I_{b+c,a+d} \end{aligned} \tag{13}$$

where

$$I_{s,t} = I_{t,s} = -\frac{1}{2}[1 + (-1)^{s+t}]\frac{e^2}{L}\pi^{-1}$$
$$\times \{(s+t)^{-1}[\mathrm{Si}(s\pi) + \mathrm{Si}(t\pi)] + (s-t)^{-1}[\mathrm{Si}(s\pi) - \mathrm{Si}(t\pi)]\} \tag{14}$$

for any $s \neq t$;

$$I_{t,t} = -\frac{e^2}{L}(t\pi)^{-1}\mathrm{Si}(t\pi) - \frac{e^2}{L}\ln(\pi t) - \frac{e^2}{L}\gamma; \tag{15}$$

$$I_{0,0} = -2\frac{e^2}{L}; \tag{16}$$

$\gamma = 0.5772157$ is the Euler constant.

With the convergent expressions (11) and (12), it is easy to perform the programme outlined in Sect. 1. The energy differences entering the expression (9) for the perturbation energy are simply

$$\Delta E^{(0)} = (b^2 - a^2)\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2} \tag{17}$$

in the case of one-electron $a \to b$ excitations, and

$$\Delta E^{(0)} = (c^2 + d^2 - a^2 - b^2)\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2} \tag{17a}$$

in the case of two-electron $a, b \to c, d$ excitations.

3 Electron excitation energy of the one-dimensional electron gas influenced by the electron correlations

The first, rather fundamental, question which we like to answer here is the sequence of energy levels in the electron gas in the case when the Coulomb electron interaction is included. In the absence of this interaction the answer is rather simple: for a one-electron excitation from the level N to the level $N + A$, where $A \geqslant 1$, the excitation energy given by Eq. (17) is

$$\Delta E^{(0)}_{N\to N+A} = [(N + A)^2 - N^2]\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2} \tag{18}$$

and this is a positive number for any $A \geqslant 1$. A question may arise whether $\Delta E^{(0)}_{N\to N+A} > 0$ holds also in the presence of the electron correlations. This question can be examined in dependence on the size of the parameters N, A, L, as well as the size of the charge e. In the first step we can examine the extension of Eq. (18) given in the Hartree–Fock (HF) approximation. Thus,

$$\Delta E^{\mathrm{HF}}_{N\to N+A} = \Delta E^{(0)}_{N\to N+A} + \Delta E^{(1)}_{N\to N+A}, \tag{19}$$

where

$$\Delta E^{(1)}_{N\to N+A} = E^{(1)}(N + A) - E^{(1)}(N)$$
$$= \sum_{j=1,2,3,\ldots,N-1} (J_{N+A,j} - K_{N+A,j} - J_{N,j} + K_{N,j}); \tag{20}$$

the differences $J_{N+A,j} - K_{N+A,j}$ and $J_{N,j} - K_{N,j}$ can be readily calculated for any j by Eq. (13).

In the second step, the problem can be examined in terms of the second-order perturbation theory:

$$\Delta E^{(\mathrm{HFcorr})}_{N\to N+A} = \Delta E^{(\mathrm{HF})}_{N\to N+A} + E^{(2)}_{N+A} - E^{(2)}_{N}. \tag{21}$$

Here we have

$$E^{(2)}_{N} = \sum_{\lambda} \frac{|U_{N\lambda}|^2}{E^{(0)}_{N} - E^{(0)}_{\lambda}} = E^{(2)}_{N,1\mathrm{el}} + E^{(2)}_{N,2\mathrm{el}} \tag{22}$$

and a similar expression holds for $E^{(2)}_{N+A}$. The part of the sum (22) corresponding to the case of the one-electron excitations becomes

$$E^{(2)}_{N,1\mathrm{el}} = \sum_{a=1}^{N} \sum_{M} \left\{ \sum_{c} \left[\left\langle ac \left| \frac{e^2}{r_{12}} \right| Mc \right\rangle - \left\langle ac \left| \frac{e^2}{r_{12}} \right| cM \right\rangle \right] \right\}^2 \times \left[\frac{\hbar^2}{2m_\mathrm{e}} \frac{\pi^2}{L^2} (a^2 - M^2) \right]^{-1}. \tag{23}$$

Here $a, c = 1, 2, \ldots, N$, $c \neq a$ and $M = N+1, N+2, \ldots$. The remaining part of Eq. (22) which corresponds to the two-electron excitations is

$$E^{(2)}_{N,2\mathrm{el}} = \frac{1}{4} \sum_{a} \sum_{b} \sum_{c} \sum_{d} \left[\left\langle ab \left| \frac{e^2}{r_{12}} \right| cd \right\rangle - \left\langle ab \left| \frac{e^2}{r_{12}} \right| dc \right\rangle \right]^2 \times \left[\frac{\hbar^2}{2m_\mathrm{e}} \frac{\pi^2}{L^2} (a^2 + b^2 - c^2 - d^2) \right]^{-1}; \tag{24}$$

where $a, b = 1, 2, \ldots, N$, $b \neq a$, and $c, d = N+1, N+2, \ldots, c \neq d$.

The expressions (23) and (24) also hold for the corresponding terms of

$$E^{(2)}_{N+A} = E^{(2)}_{N+A,1\mathrm{el}} + E^{(2)}_{N+A,2\mathrm{el}}. \tag{25}$$

$E^{(2)}_{N+A,1\mathrm{el}}$ is given by the expression (23) for $a, c = 1, 2, \ldots, N-1, N+A, c \neq a$ and $M = N, N+1, \ldots, N+A-1, N+A+1, N+A+2, \ldots$. On the other hand $E^{(2)}_{N+A,2\mathrm{el}}$ can be calculated using (24) for $a, b = 1, 2, \ldots, N-1, N+A, a \neq b$ and $c, d = N, N+1, \ldots, N+A-1, N+A+1, N+A+2, \ldots, c \neq d$. In Fig. 1 we plot the contributions to the total energy per electron minus $(\hbar^2/2m_\mathrm{e})u_{01}^2$ [see Eq. (1)] calculated for systems having $N \geqslant 2$, versus N; Fig. 2a represents the contributions to excitation energies for $N = 2$ system calculated for different approximations. In Table 1 the excitation energies for $N = 5$ system are given.

3.1 Comparison with the excitation energies of two-spin one-dimensional system. Virial theorem

The excitation energies of Sect. 3 obtained in the case of one-spin particles filling the one-electron levels can be compared, to some extent, with similar excitation

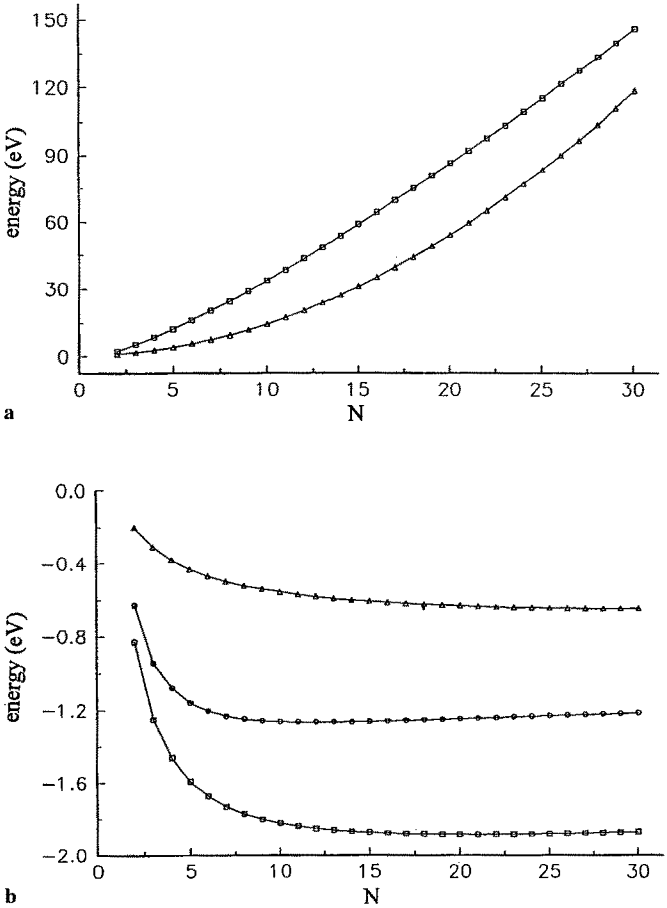
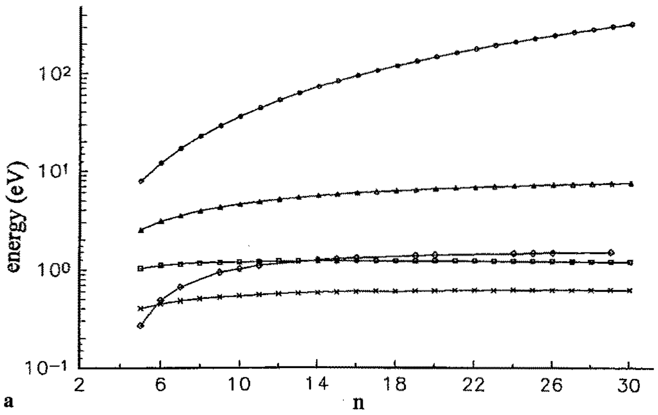
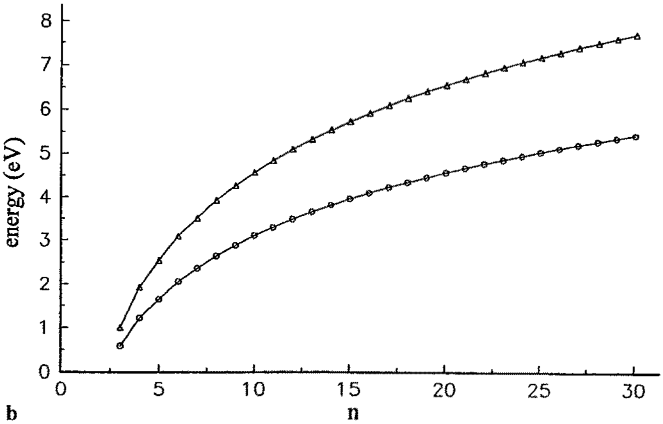


Fig. 1a,b. Energy contribution (in eV) calculated per one particle [minus $(\hbar^2/2m_e)\, u_{01}^2$ – see Eq. (1)] for N-particle Coulomb-interacting one-dimensional systems plotted vs. N;$L = 10^{-9}$ m. (a) energy $E^{(0)}$ – triangles; energy $E^{(1)}$ – squares. The sum $E^{(0)} + E^{(1)}$ gives the Hartree–Fock energy per one particle. (b) Energy $E_{1el}^{(2)}$ – circles; energy $E_{2el}^{(2)}$ – triangles. Energy $E^{(2)}$ – represented by squares is the sum $E_{1el}^{(2)} + E_{2el}^{(2)}$

energies of the model in which the one-electron levels are doubly occupied by electron particles having two opposite spins. This last model can represent a real many-electron system. The divergencies in the Coulomb and exchange interaction energies obtained usually in this case for the situation of $R \to 0$ can be avoided on condition that all electron levels are doubly occupied and in the course of an excitation the electron pair occupying originally some level a is excited to some level b. Then the excitation energy of one electron from a to b calculated in the framework of the model given in Sect. 3 can be compared with a half of the excitation energy of electron pair promoted from a to b calculated in a two-spin model. The zero-order excitation energy $\Delta E^{(0)}$, when taken per one electron, is evidently the same for both kinds of models, so we focus our attention on the electron interaction contribution $\Delta E^{(1)}$ to the excitation energy. For the model of Sect. 3 this energy contribution



a



b

Fig. 2a. Contributions (in eV) to the excitation energy of states $\{1, n\}$ of 2-particle one-dimensional system plotted vs. index n of the excitation level; $L = 10^{-9}$ m. The excitation energy is the energy difference between $\{1, n\}$ and $\{1, 2\}$. Energy $\Delta E^{(0)}$ – circles; $\Delta E^{(1)}$ – triangles; $\Delta E^{(2)}_{1\text{el}}$ – squares; $\Delta E^{(2)} = E^{(2)}_{1\text{el}} + E^{(2)}_{2\text{el}}$ – rhombs; crosses represent a negative difference between the electron–core interaction energy in $\{1, n\}$ and $\{1, 2\}$

Fig. 2b. $\Delta E^{(1)}$ is compared with $\Delta \bar{E}^{(1)}$ which is a half of the electron interaction contribution to the excitation energy of a real (two-spin) system obtained in the case when both levels 1 and 2 are occupied by electron pairs in the system in its ground state and the pair located originally on level 2 is excited to level n; see Sect. 3.1. Upper line: $\Delta E^{(1)}$ vs. n; lower line: $\Delta \bar{E}^{(1)}$ vs. n

is given in Eq. (20), whereas in a two-spin model a half of this energy contribution is

$$\Delta \bar{E}^{(1)}_{N \to N+A} = \sum_{j=1,2,3,\ldots,N-1} (2J_{N+A,j} - 2J_{N,j} - K_{N+A,j} + K_{N,j}) + \frac{1}{2}(J_{N+A,N+A} - J_{N,N}); \tag{26}$$

Table 1. Contributions to the excitation energy (in eV) of a 5-particle system calculated for different L (in 10^{-10} m) coming from different approximations of the perturbation theory.

	$L = 1$	$L = 10$
Excited state $\{1,2,3,4,6\}$		
$\Delta E^{(0)}$	4.14×10^2	4.14
$\Delta E^{(1)}$	2.46×10	2.46
$\Delta E^{(2)}_{1\mathrm{el}}$	1.07×10^{-1}	1.07×10^{-1}
$\Delta E^{(2)}_{2\mathrm{el}}$	-9.22×10^{-1}	-9.22×10^{-1}
$\Delta E^{(\mathrm{HFcorr})}$	4.16×10^2	5.79
$\Delta E^{c(1)}$	-1.16	-1.2×10^{-1}
$\Delta E^{c(2)}$	0.43×10^{-2}	0.43×10^{-2}
Excited state $\{1,2,3,4,15\}$		
$\Delta E^{(0)}$	7.52×10^3	7.52×10
$\Delta E^{(1)}$	1.39×10^2	1.39×10
$\Delta E^{(2)}_{1\mathrm{el}}$	3.37×10^{-1}	3.37×10^{-1}
$\Delta E^{(2)}_{2\mathrm{el}}$	-2.36×10^{-1}	-2.36×10^{-1}
$\Delta E^{(\mathrm{HFcorr})}$	7.66×10^3	8.92×10
$\Delta E^{c(1)}$	-4.67	-4.7×10^{-1}
$\Delta E^{c(2)}$	-1.5×10^{-1}	-1.5×10^{-1}

State $\{1,2,3,4,5\}$ is the ground state. First row: $\Delta E^{(0)}$ – zero-order perturbation energy; second row: $\Delta E^{(1)}$ – first-order correction to the Coulomb perturbation energy; third row: $\Delta E^{(2)}_{1\mathrm{el}}$ – the second-order correction to the Coulomb perturbation energy obtained for the one-particle excitations; fourth row: $\Delta E^{(2)}_{2\mathrm{el}}$ – the second-order correction to the Coulomb perturbation energy obtained for the two-particle excitations; the fifth row is the total of $\Delta E^{(0)} + \Delta E^{(1)} + \Delta E^{(1)}_{1\mathrm{el}} + \Delta E^{(2)}_{2\mathrm{el}}$ represented by $\Delta E^{(\mathrm{HFcorr})}$. The sixth and seventh row are the electron-core interaction energies calculated in the first and the second order of the perturbation theory, respectively (see Sect. 3)

here the electron pair is promoted from the top occupied level N to the level $N + A$. For the case when $N = 2$ and $A = 1, 2, \ldots, 28$ the $\Delta \bar{E}^{(1)}_{N\to N+A}$ given in Eq. (26) is compared with $\Delta E^{(1)}_{N\to N+A}$ from Eq. (20) in Fig. 2b. We find that $\Delta \bar{E}^{(1)}_{N\to N+A}$ is smaller than $\Delta E^{(1)}_{N\to N+A}$ for any $A \geqslant 1$. However, the ratio $(\Delta E^{(1)}_{N\to N+A} - \Delta \bar{E}^{(1)}_{N\to N+A}) / \Delta E^{(1)}_{N\to N+A}$ decreases with the increase of A and does not exceed 40% for small A.

It seems of interest to examine also the virial theorem in our model. For three dimensions this theorem states that [108, 109]

$$2E_{\mathrm{kin}} + E_{\mathrm{pot}} = \mu P V, \tag{27}$$

where

$$P = -\frac{\partial (E_{\mathrm{kin}} + E_{\mathrm{pot}})}{\partial V} \tag{28}$$

is the electron gas pressure at the boundary of the electron gas volume V and $\mu = \mu^{(3)} = 3$. For a one-dimensional electron gas enclosed in a cylindrical potential box of volume $V = \pi R^2 L$ we assume that the radius R of the box remains unchanged, so that

$$P = -\frac{\partial(E_{\mathrm{kin}} + E_{\mathrm{pot}})}{\pi R^2 \partial L}. \tag{29}$$

In our model we have

$$E_{\mathrm{kin}} = E^{(0)} = \frac{A}{L^2}, \qquad E_{\mathrm{pot}} = E^{(1)} = \frac{B}{L}, \tag{30}$$

where A and B are independent of the box length L. Thus, we obtain

$$2E_{\mathrm{kin}} + E_{\mathrm{pot}} = -\frac{\partial(E_{\mathrm{kin}} + E_{\mathrm{pot}})}{\partial L} L = PV. \tag{31}$$

In effect, Eq. (27) is satisfied also for one dimension on condition that $\mu = \mu^{(1)} = 1$ and E_{pot} is limited to $E^{(1)}$; the inclusion of $E^{(2)}$ into E_{pot} cancels the equality given in Eq. (31).

3.2 The positive background and its influence

We assume the Coulomb-interacting particles in the box have a negative charge, so, in order to neutralize it, a positive background distributed uniformly within the box volume should be taken into account. If Z positive elementary charges fill uniformly a cylindrical box volume neutralizing Z electrons present within the box, the density of the positive charge is

$$e\rho^{(+)} = Ze(\pi R^2 L)^{-1}, \tag{32}$$

so that the Coulomb potential energy of the interaction with one electron charge given by state (3) is

$$E_k^{c(1)} = -Ze^2(\pi R^2 L)^{-1} \iint \frac{\varphi_k^*(\boldsymbol{r})\varphi_k(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}_+|} \, \mathrm{d}\boldsymbol{r}_+ \, \mathrm{d}\boldsymbol{r}; \tag{33}$$

here the variable $\boldsymbol{r}_+$ refers to a volume element of the positive background; the integrals over $\boldsymbol{r}$ and $\boldsymbol{r}_+$ are extended over the box volume. A difficulty in the calculation of Eq. (33) is that the integral entering Eq. (33) diverges at $R \to 0$. Fortunately, we can calculate a convergent difference at $R \to 0$ between two first-order electron-core interaction energies (33) for two different electron states, say $k = a$ and $k = b$. We obtain

$$\Delta E_{a\to b}^{c(1)} = -Z(I_{0,2b} - I_{0,2a}). \tag{34}$$

The second-order perturbation energy expression for the core interaction with an electron at the electron level k is equal to

$$\Delta E_k^{c(2)} = \sum_{m \neq k} \left| \left\langle k \left| \frac{Ze^2}{|\boldsymbol{r} - \boldsymbol{r}_+|} \right| m \right\rangle \right|^2 \left[\frac{\hbar^2}{2m_{\mathrm{e}}} \frac{\pi^2}{L^2} (k^2 - m^2) \right]^{-1}, \tag{35}$$

where

$$\left\langle k \left| \frac{Ze^2}{|r - r_+|} \right| m \right\rangle = Z\left\{ I_{0,|k-m|} \frac{1}{2} [(-1)^{|k-m|} + 1] - I_{0,|k+m|} \frac{1}{2} [(-1)^{k+m} + 1] \right\} \tag{36}$$

is a convergent result. Hence, also Eq. (35) converges since $m \neq k$.

In Table 1 we present the data obtained with the aid of the formulae (34) and (35).

3.3 Accuracy of the perturbation calculation

The perturbation method applied in the present paper is typical for the Rayleigh–Schrödinger (RS) theory and we may compare its accuracy with a more sophisticated approach in which at least a part of perturbation energies of the infinite order is included in the first few perturbation terms. Such a method applies shifted-energy denominators in which the perturbation energy of a lower order, e.g. that given by the Coulomb interactions, enters the energy denominators; see [110] and cf. also [111]. The RS perturbation series is obtained when the shifted-energy denominators are expanded as the power series of the perturbation parameter [110]. The accuracy of both methods, viz. the RS method and that having shifted-energy denominators, can be compared for different perturbation orders by solving numerically the Löwdin's equations [112], viz.

$$0 = -\mathscr{E} + E_n^{(0)} + E_n^{(1)} + \sum_p \frac{U_{np}U_{pn}}{\mathscr{E} - E_p^{(0)}} \tag{37}$$

for the first perturbation order,

$$0 = -\mathscr{E} + E_n^{(0)} + E_n^{(1)} + \sum_p \frac{U_{np}U_{pn}}{\mathscr{E} - E_p^{(0)}} + \sum_p \sum_q \frac{U_{np}U_{pq}U_{qn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})} \tag{37a}$$

for the second perturbation order,

$$0 = -\mathscr{E} + E_n^{(0)} + E_n^{(1)} + \sum_p \frac{U_{np}U_{pn}}{\mathscr{E} - E_p^{(0)}} + \sum_p \sum_q \frac{U_{np}U_{pq}U_{qn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})} + \sum_p \sum_q \sum_r \frac{U_{np}U_{pq}U_{qr}U_{rn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})(\mathscr{E} - E_r^{(0)})} \tag{37b}$$

for the third perturbation order, and

$$0 = -\mathscr{E} + E_n^{(0)} + E_n^{(1)} + \sum_p \frac{U_{np}U_{pn}}{\mathscr{E} - E_p^{(0)}} + \sum_p \sum_q \frac{U_{np}U_{pq}U_{qn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})} + \sum_p \sum_q \sum_r \frac{U_{np}U_{pq}U_{qr}U_{rn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})(\mathscr{E} - E_r^{(0)})} + \sum_p \sum_q \sum_r \sum_s \frac{U_{np}U_{pq}U_{qr}U_{rs}U_{sn}}{(\mathscr{E} - E_p^{(0)})(\mathscr{E} - E_q^{(0)})(\mathscr{E} - E_r^{(0)})(\mathscr{E} - E_s^{(0)})} \tag{37c}$$

which is the equation for the fourth order of the perturbation, etc. The solutions for $\mathscr{E}$ obtained from Eqs. (37)–(37c) are compared with:

(i) the RS perturbed energies, viz. $E^{\mathrm{RS}(1)}$, $E^{\mathrm{RS}(2)}$, $E^{\mathrm{RS}(3)}$, $E^{\mathrm{RS}(2)}$, $E^{\mathrm{RS}(4)}$ of state n calculated up to the first, second, third and fourth perturbation order of the RS theory correspondingly (see e.g. [113]);

(ii) the modified perturbed energies [110] which for the perturbation orders 1 and 2 are identical with $E^{\mathrm{RS}(1)}$ and $E^{\mathrm{RS}(2)}$ but for the perturbation order 3 read

$$E^{(3)} = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \sum_p \sum_q \frac{U_{np} U_{pq} U_{qn}}{(E_n^{(0)} + E_n^{(1)} - E_p^{(0)})\,(E_n^{(0)} + E_n^{(1)} - E_p^{(0)})}, \tag{38}$$

and for the perturbation order 4 read

$$\begin{aligned} E^{(4)} = {} & E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \\ & + \sum_p \sum_q \frac{U_{np} U_{pq} U_{qn}}{(E_n^{(0)} + E_n^{(1)} + E_n^{(2)} - E_p^{(0)})\,(E_n^{(0)} + E_n^{(1)} - E_n^{(2)} - E_p^{(0)})} \\ & + \sum_p \sum_q \sum_r \frac{U_{np} U_{pq} U_{qr} U_{rn}}{(E_n^{(0)} + E_n^{(1)} - E_p^{(0)})\,(E_n^{(0)} + E_n^{(1)} - E_q^{(0)})\,(E_n^{(0)} + E_n^{(1)} - E_r^{(0)})}. \end{aligned} \tag{38a}$$

The expressions in Eqs. (38) and (38a) are obviously different from $E^{\mathrm{RS}(3)}$ and $E^{\mathrm{RS}(4)}$; moreover $E^{\mathrm{RS}(1)} = E_n^{(0)} + E_n^{(1)}$ and $E^{\mathrm{RS}(2)} = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$. For the further perturbation orders, viz., $a > 4$, the terms $E^{(a-2)}$, $E^{(a-3)}$, … enter the denominators of the terms representing $E^{(a)}$ [110]. In Table 2 we compare the accuracy of $E^{\mathrm{RS}(3)}$ and $E^{\mathrm{RS}(4)}$ with that of $E^{(3)}$ and $E^{(4)}$ by substituting, respectively,

$$\mathscr{E} = E^{\mathrm{RS}(3)}, E^{\mathrm{RS}(4)} \tag{39}$$

and

$$\mathscr{E} = E^{(3)}, E^{(4)} \tag{39a}$$

into the third-order equation (37b) and the fourth-order equation (37c). For a smaller L the perturbation procedure is, in general, better justified than for a larger L. We find in this case that

$$|\Delta E^{\mathrm{RS}(a)}| < |\Delta E^{(a)}| \tag{40}$$

both for $a = 3$ and $a = 4$ which implies a better accuracy of the RS series than the series having the perturbation energies in denominators.

4 One-dimensional gas modified by the Coulomb correlations

A well-known result for the uncorrelated density of the electron gas is that it is practically constant except for the area which is very close to the gas boundary. This holds, of course, also in the case of the one-dimensional gas; see e.g. [114]. Our purpose is to examine whether this result can be modified by the Coulomb

Table 2. Comparison of the accuracy of the perturbation energy obtained from the RS perturbation series and a modified perturbation series having the lower-order perturbation terms in denominators [110].

Perturbation order 1

L	$E^{RS(1)} = E^{(1)}$	$\Delta E^{RS(1)} = \Delta E^{(1)}$
10^{-10}	$2.359308452 \times 10^{2}$	-1.90
10^{-11}	$1.928065701 \times 10^{4}$	-1.68

Perturbation order 2

L	$E^{RS(2)} = E^{(2)}$	$\Delta E^{RS(2)} = \Delta E^{(2)}$
10^{-10}	$2.342727841 \times 10^{2}$	2.09×10^{-1}
10^{-11}	$1.927899895 \times 10^{4}$	1.38×10^{-2}

Perturbation order 3

L	$E^{RS(3)}$	$\Delta E^{RS(3)}$
10^{-10}	$2.344040688 \times 10^{2}$	-2.89×10^{-2}
10^{-11}	$1.927901208 \times 10^{4}$	-9.97×10^{-5}

L	$E^{(3)}$	$\Delta E^{(3)}$
10^{-10}	$2.343680596 \times 10^{2}$	7.25×10^{-3}
10^{-11}	$1.927901177 \times 10^{4}$	2.10×10^{-4}

Perturbation order 4

L	$E^{RS(4)}$	$\Delta E^{RS(4)}$
10^{-10}	$2.343956148 \times 10^{2}$	5.35×10^{-3}
10^{-11}	$1.927901199 \times 10^{4}$	6.21×10^{-7}

L	$E^{(4)}$	$\Delta E^{(4)}$
10^{-10}	$2.344155964 \times 10^{2}$	-1.47×10^{-2}
10^{-11}	$1.927901201 \times 10^{4}$	-1.55×10^{-5}

The third and the fourth perturbation orders are examined for the Coulomb interaction between an electron pair taken as a perturbation: ΔE^{RS} are the numbers obtained for the right-hand side of Eqs. (37b) and (37c) when $E^{RS(3)}$ and $E^{RS(4)}$ are substituted, respectively, for $\mathcal{E}$, whereas ΔE are the numbers obtained for the right-hand side of Eqs. (37b) and (37c) when $E^{(3)}$ and $E^{(4)}$ from Eqs. (38) and (38a) are substituted, respectively, for $\mathcal{E}$. For the sake of comparison the ΔE equal to the right-hand side of Eqs. (37) and (37a) in the case when the lower-order energies $E^{RS(1)} = E^{(1)}$ and $E^{RS(2)} = E^{(2)}$ are substituted for $\mathcal{E}$ are also given. L is the box length (in m); all energies are in eV correlations. In other words our question is whether for a given particle number N and the elementary charge e one can find such L that the originally uniform electron density in the gas can be expected to be considerably disturbed. In this search we are guided by the Wigner's result for a distance characteristic for the electron lattice obtained in the three-dimensional gas at very low densities as well as the existence of the Mott transition between a metallic and a non-metallic state.

A measure of the correlation influence on the electron distribution can be represented by the change of the normalization coefficient of the perturbed wave function. For example, let us consider the wave function $|N\rangle$ of the ground state of the gas; the change of the normalization coefficient of $|N\rangle$ is given by the interaction elements between $|N\rangle$ and all possible excited states $|M\rangle$ of the gas. If we assume that all unperturbed determinantal wave functions are normalized to 1, then the change of the normalization coefficient of $|N\rangle$ expressed in terms of the second-order perturbation theory is given by the formula

$$\Delta^{(2)} = \langle N^{\mathrm{corr}} | N^{\mathrm{corr}} \rangle - 1 = \sum_M \frac{|U_{NM}|^2}{(E_N^{(0)} - E_M^{(0)})^2}; \tag{41}$$

$|M\rangle \neq |N\rangle$ (see e.g. [115]). This formula can be considerably simplified if we note that the matrix elements U_{NM} vanish when $|M\rangle$ and $|N\rangle$ differ in the occupation number of more than two one-electron levels. If $|N\rangle$ and $|M\rangle$ differ in the occupation of only one electron level then the corresponding term in Eq. (41) can be calculated according to Eq. (11); if $|N\rangle$ and $|M\rangle$ differ in the occupation of two levels, U_{NM} is given by Eq. (12). In effect, the sum (41) can be separated into two parts coming from the one-electron and two-electron excitations, similarly to the energy expressions given above.

Let us represent formally a contribution to $\Delta^{(2)}$ in Eq. (41) coming from the level i by

$$\Delta_i^{(2)} = \Delta_{i,1\mathrm{el}}^{(2)} + \tfrac{1}{2}\Delta_{i,2\mathrm{el}}^{(2)}, \tag{42}$$

where again we have the terms coming from the one-electron and two-electron excitations;

$$\Delta^{(2)} = \sum_i \Delta_i^{(2)}. \tag{42a}$$

The factor $\frac{1}{2}$ in the last term in (42) takes into account the fact that only a half of the contributions $\Delta_{i,2\mathrm{el}}^{(2)}$ should be attributed to the level i and the remainder to the other levels, i.e. $1, 2, \ldots, i-1, i+1, \ldots, N$. We can be interested, for example, in a contribution to the correlation change $\Delta_i^{(2)}$ given by the lowest electron level represented by $\varphi_1(\boldsymbol{r})$ [see Eq. (3) $i = k = 1$]. If N subsequent levels $i = 1, 2, \ldots, N$ in the ground state are singly occupied by N electrons then

$$\Delta_{1,1\mathrm{el}}^{(2)} = \sum_M \left\{ \sum_c \left[\left\langle 1c \left| \frac{e^2}{r_{12}} \right| Mc \right\rangle - \left\langle 1c \left| \frac{e^2}{r_{12}} \right| cM \right\rangle \right] \right\}^2 \left\{ \frac{\hbar^2}{2m_e} \frac{\pi^2}{L^2} [1^2 - M^2] \right\}^{-2}, \tag{43}$$

$$\Delta_{1,2\mathrm{el}}^{(2)} = \frac{1}{2} \sum_b \sum_c \sum_d \left[\left\langle ab \left| \frac{e^2}{r_{12}} \right| cd \right\rangle - \left\langle ab \left| \frac{e^2}{r_{12}} \right| dc \right\rangle \right]^2 \times \left[\frac{\hbar^2}{2m_e} \frac{\pi^2}{L^2} (a^2 + b^2 - c^2 - d^2) \right]^{-2}. \tag{44}$$

Table 3. Coulomb correlations $\Delta^{(2)}_{i,1\mathrm{el}}$ and $\Delta^{(2)}_i$ calculated for individual levels of the 5-particle system and their sum $\Delta^{(2)}$ [Eqs. (43)–(45)]; the total core-correlated $\Delta^{(2)}_{\mathrm{core}}$ [Eq. (45)]

	$\Delta^{(2)}_{i,1\mathrm{el}}$	$\Delta^{(2)}_i$	$\Delta^{(2)}_{\mathrm{core}}$
Ground state: $\{1,2,3,4,5\}$			
$i=1$	2.66×10^{-1}	5.47×10^{-1}	
$i=2$	3.29	3.86	
$i=3$	3.45	4.61	
$i=4$	5.00×10	5.24×10	
$i=5$	1.04×10	1.27×10	
$\Delta^{(2)}$	6.74×10	7.41×10	6.19×10^{-4}
Excited state: $\{1,2,3,4,6\}$			
$i=1$	2.21	2.67	
$i=2$	1.25×10^{-1}	9.62×10^{-1}	
$i=3$	5.77×10	5.94×10	
$i=4$	3.67	1.13×10	
$i=6$	9.99	1.87×10	
$\Delta^{(2)}$	7.37×10	9.30×10	6.79×10^{-4}
Excited state: $\{1,2,3,4,15\}$			
$i=1$	2.32	3.17	
$i=2$	3.37	5.39	
$i=3$	6.25×10	7.09×10	
$i=4$	1.30×10	2.79×10	
$i=15$	9.06	2.87×10	
$\Delta^{(2)}$	9.03×10	1.36×10^{2}	9.24×10^{-4}

Comparison between the levels of the ground and excited states; index i labels the levels occupied in the system; $L = 10^{-8}\,\mathrm{m}$

Here $c = 2, 3, \ldots, N$ and $M = N+1, N+2, \ldots$ for expression (43), whereas $a = 1, b = 2, 3, \ldots, N$ and $c, d = N+1, N+2, \ldots, c \neq d$ for expression (44).

In the same way we can calculate Eq. (42) for all other i, viz., $i \neq 1$, in the case of the gas being in its ground state. But the same problem can be also stated when the gas is in an excited state represented, for example, by a shift of one electron from the level N to some level $N + A$. If we focus our attention on a one-electron level i, this calculation enables us to examine how strongly some one-electron excitation $N \to N + A$ can influence the electron distribution $\varphi_i^* \varphi_i$. In Table 3 we represent $\Delta^{(2)}_{i,1\mathrm{el}}$ and $\Delta^{(2)}_i$ calculated for different i's and different states of a five-particle system.

A separate problem is polarization of the electron charge density by a uniform positive core; see Sect. 3.2. In this case, instead of Eq. (41) we have

$$\Delta^{(2)}_{\mathrm{core}} = \langle N^{\mathrm{core}} | N^{\mathrm{core}} \rangle - 1 = \sum_M \frac{|U^{\mathrm{core}}_{NM}|^2}{(E^{(0)}_N - E^{(0)}_M)^2}, \tag{45}$$

where U^{core}_{NM} is equal to the matrix element given in Eq. (36) on condition we put $k = N$ and $m = M$. The data obtained for $\Delta^{(2)}_{\mathrm{core}}$ are listed in Table 3.

5 Löwdin–Tomonaga expression for the correlation between particle positions

In Sect. 4 we proposed a global insight into the correlation between particles via the calculation of the change of the normalization coefficient of the correlated wave function. For a small number of particles, say 2, we can examine also the local change of the particle density due to correlation by drawing the patterns of equal probability density in the two-dimensional space of z_1 and z_2. These patterns calculated for the correlated two-particle wave function can be compared with a similar pattern of the density given by the wave function correlated only according to the Pauli principle, viz.

$$\rho^P(z_1, z_2) = \frac{1}{2}\begin{vmatrix} \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{m\pi}{L}z_1\right), & \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi}{L}z_1\right) \\ \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{m\pi}{L}z_2\right), & \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi}{L}z_2\right) \end{vmatrix}^2 ; \qquad (46)$$

see Figs. 3 and 4. These density patterns are similar to those given a long time ago by Slater et al. [116] for a two-particle one-dimensional problem. An interesting presentation of the influence of the Coulomb correlation on the particle density can be done following Ref. [117].

For the ground state $\{1, 2\}$ of the two-particle system in which two lowest levels 1, 2 are occupied, the Coulomb correlated wave function $\psi\{1, 2\}$ can be represented by the sum of the Pauli-correlated part $\psi^{(0)}\{1, 2\}$ and the perturbation parts coming from the one-electron and two-electron excitations, viz.,

$$\psi\{1, 2\} = \psi^{(0)}\{1, 2\} + \psi^{(1)}_{1\mathrm{el}}\{1, 2\} + \psi^{(1)}_{2\mathrm{el}}\{1, 2\}, \qquad (47)$$

where

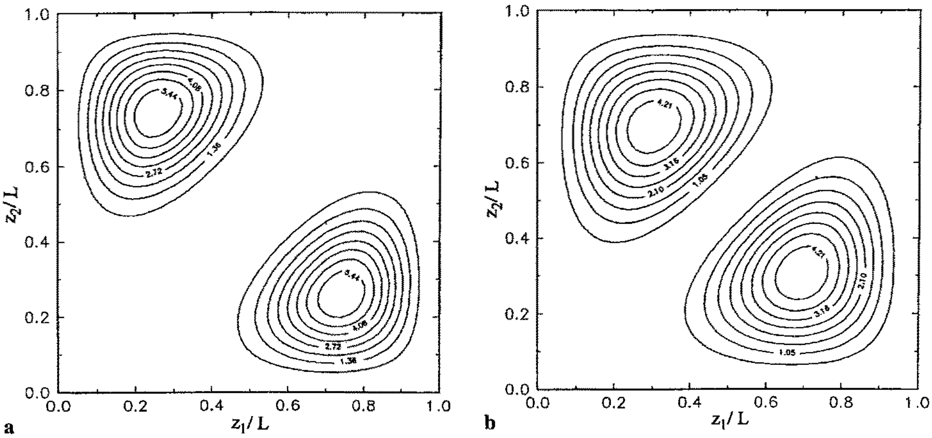
$$\psi^{(0)}\{1, 2\} = \frac{1}{\sqrt{2}}\left[\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2) - \varphi_2(\boldsymbol{r}_1)\varphi_1(\boldsymbol{r}_2)\right], \qquad (47a)$$

a part coming from the one-electron excitations is

$$\psi^{(1)}_{1\mathrm{el}}\{1, 2\} = \sum_{N=1,2}\sum_{M>2}\left[\left\langle Mc\left|\frac{e^2}{r_{12}}\right|Nc\right\rangle - \left\langle Mc\left|\frac{e^2}{r_{12}}\right|cN\right\rangle\right] \times\left[\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2}(N^2 - M^2)\right]^{-1}\psi^{(0)}\{N, M\}, \qquad (47b)$$

and a part coming from the two-electron excitations is

$$\psi^{(1)}_{2\mathrm{el}}\{1, 2\} = \frac{1}{2}\sum_{M}\sum_{M'}\left[\left\langle 12\left|\frac{e^2}{r_{12}}\right|MM'\right\rangle - \left\langle 12\left|\frac{e^2}{r_{12}}\right|M'M\right\rangle\right] \times\left[\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2}(1^2 + 2^2 - M^2 - M'^2)\right]^{-1}\psi^{(0)}\{M, M'\}, \qquad (47c)$$



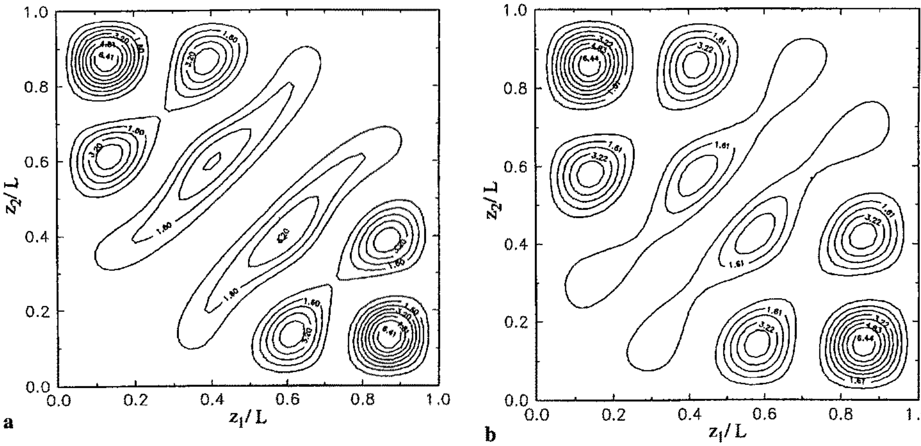
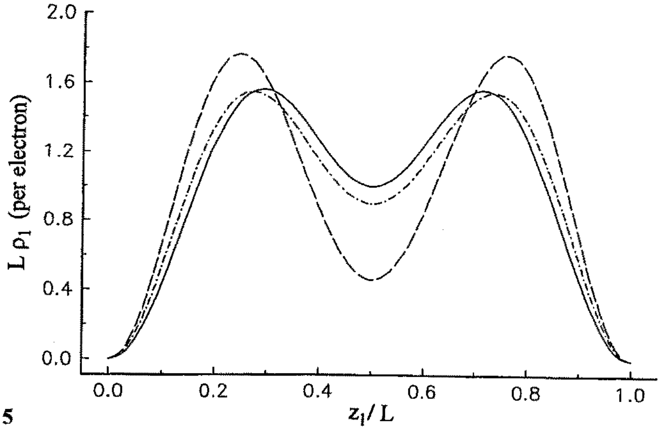


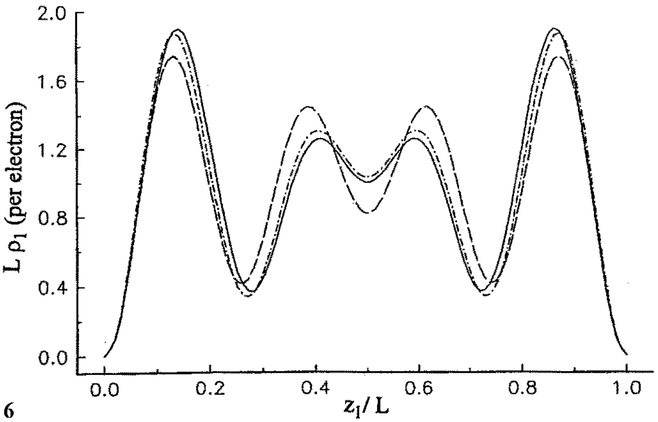
Fig. 3 and 4. Maps of the 2-particle Coulomb-correlated density $L|\psi\{m, n\}|^2$ (Figs. 3a and 4a) and Pauli correlated (Coulomb uncorrelated) density $L|\psi^{(0)}\{m, n\}|^2$ (Figs. 3b and 4b) plotted vs. $L^{-1}z_1$ and $L^{-1}z_2$ for different states $\{m, n\}$; L is taken equal to 5×10^{-10} m. The wave function $\psi\{m, n\}$ is the Coulomb-correlated wave function for the state $\{m, n\}$, whereas $\psi^{(0)}\{m, n\}$ is the Pauli-correlated (Coulomb uncorrelated) wave function for the state $\{m, n\}$; integers m, n label the occupied levels. Figs. 3a,b – state $\{1, 2\}$; Figs. 4a,b – state $\{3, 4\}$

($M, M' > 2$, $M \neq M'$). In the curly brackets we have the level symbols; for $N = 1$ we have a common index $c = 2$ in the ground state $|N\rangle$ and the excited states $|M\rangle$ (transitions $N = 1 \rightarrow M > 2$), whereas $c = 1$ for transitions from $N = 2 \rightarrow M > 2$. From any two-particle wave function $\psi(z_1, z_2)$ we can obtain the one-particle density operator [117]:

$$\rho_1(z_1) = \int |\psi(z_1, z_2)|^2 \, dz_2 \tag{48}$$

by integrating over the variable z_2. The Coulomb correlated and Coulomb uncorrelated one-particle density obtained according to Eq. (48) is compared for different





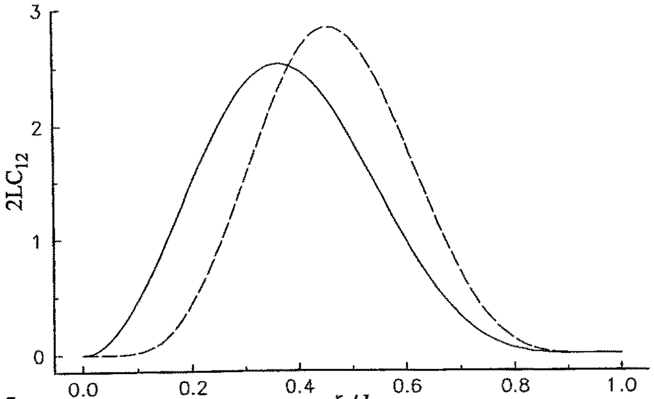
Figs. 5 and 6. The one-particle density $L\rho_1(z_1)$ obtained from the Coulomb-correlated wave functions $\psi\{m,n\}$ (dashed curves), core-correlated wave functions (dashed–dot curves), and the Coulomb-and-core uncorrelated (Pauli-correlated) wave functions $\psi^{(0)}\{m,n\}$ (continuous curves) for different states $\{m,n\}$; see Eq. (48). The integers m, n label the occupied levels. Fig. 5 – state $\{1,2\}$, Fig. 6 – state $\{3,4\}$

states in Figs. 5 and 6. The two-particle probability density for the wave function $\psi(z_1, z_2)$ is equal to the diagonal two-particle density matrix [118]:

$$\rho_2(z_1, z_2) = |\psi(z_1, z_2)|^2. \tag{49}$$

This density matrix is defined as the density of probability (in the two-dimensional space of z_1 and z_2) that the first electron is at z_1, while the other is at z_2; the term $\psi(z_1, z_2)$ can be either the Pauli correlated or Coulomb correlated wave function. Thus the average density of probability that two particles are at distance ξ is given by

$$C_{12}(\xi) = \iint_{0 \leqslant z_1 \leqslant L, 0 \leqslant z_2 \leqslant L, z_2 = z_1 + \xi} dz_1\, dz_2\, \rho_2(z_1, z_2) = \int_0^L dz_1 |\psi(z_1, z_1 + \xi)|^2. \tag{50}$$



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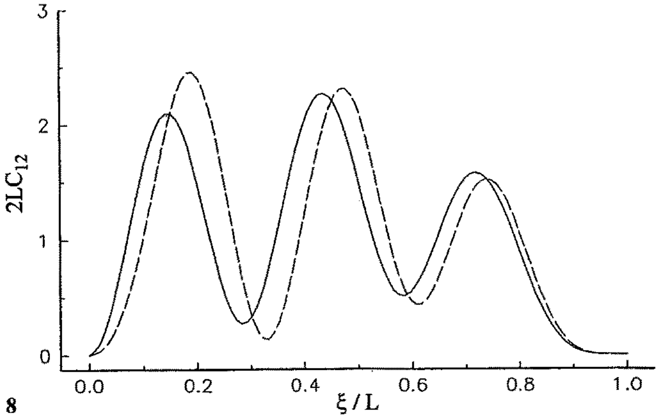

8

Figs. 7 and 8. Density integral performed along the line parallel to the diagonal line $z_1 = z_2$ for the Coulomb correlated (dashed curve) and Coulomb uncorrelated (continuous curve) 2-particle density; see (50). The density $2LC_{12}(\xi)$ is plotted as a function of the $L^{-1}\xi$ where ξ is the distance of the integration line from the diagonal $z_1 = z_2$. Fig. 7 – state $\{1, 2\}$, Fig. 8 – state $\{3, 4\}$. $L = 5 \times 10^{-10}$ m

In Figs. 7 and 8 we represent the Pauli correlated and the Coulomb correlated $C_{12}(\xi)$. It can be easily checked that in any case the probability density $C_{12}(\xi)$ fulfills the required relation

$$\int_{-L}^{L} C_{12}(\xi)\mathrm{d}\xi = 1. \tag{51}$$

Let us also note that $C_{12}(\xi)$ vanishes at $\xi = 0$, which is an expected result due to the asymmetry of any wave function $\psi(z_1, z_2)$.

In Fig. 9 we compare the correlated and uncorrelated density of the five-particle problem. The correlated density is obtained from the formula

$$\rho_1(z_1) = \int \mathrm{d}z_2 \int \mathrm{d}z_3 \int \mathrm{d}z_4 \int \mathrm{d}z_5 \, |\psi(z_1, z_2 \ldots, z_5)|^2, \tag{52}$$

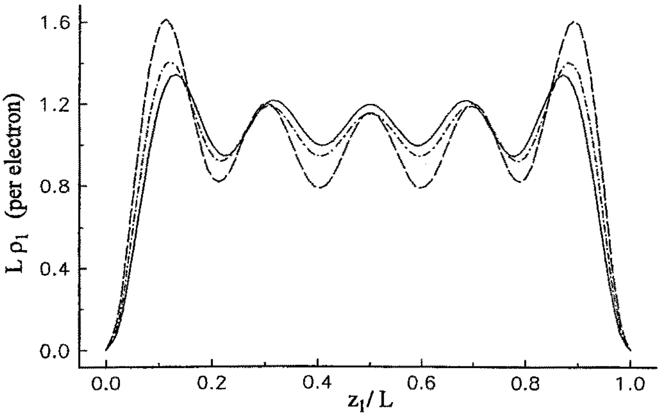

Fig. 9. The Coulomb-correlated density $L\rho_1(z)$ (dashed curve) and core-correlated density (dashed–dot curve) of 5-particle system [see Eq. (52)] compared with uncorrelated density $L\rho_1^{(0)}(z_1)$ of the same system (continuous)

where $\psi(z_1, z_2, \ldots, z_5)$ is calculated according to expression similar to that given in Eq. (47); the uncorrelated density $\rho_1^{(0)}(z_1)$ is obtained from Eq. (52) in the same way with $\psi^{(0)}(z_1, z_2, \ldots, z_5)$ substituted instead of $\psi(z_1, z_2, \ldots, z_5)$.

6 Metal–insulator transition in a Coulomb-interacting one-dimensional system

It is usually assumed that the change of a many-particle state, termed the Mott transition, occurs when a conduction electron of the metal forms a bound state with an ion in the lattice. In the case of a one-dimensional one-band model the absence of the Mott transition in an exact solution of the short-range interaction problem is pointed out in Ref. [81]. In our case of the long-range Coulomb interaction we demonstrate the behavior of the system similar to that characteristic for the Mott transition by examining the system's excitation energies.

We have the zero-order, or unperturbed, excitation energy $\Delta E^{(0)}$ of a system proportional to L^{-2}, the first-order perturbation energy due to the Coulomb repulsion proportional to L^{-1}, which together with $\Delta E^{(0)}$ gives the HF excitation energy, whereas the second-order perturbation energy due to the same repulsion, viz. $E^{(2)}$, gives a contribution $\Delta E^{(2)}$ represented by a term independent of L. Neglecting high-order terms $\Delta E^{(3)}, \Delta E^{(4)} \ldots$ we can consider the total excitation energy

$$\Delta E = \Delta E^{(0)} + \Delta E^{(1)} + \Delta E^{(2)}. \tag{53}$$

In a metallic system a usually expected situation is that

$$\Delta E = E_{\{a,c\}} - E_{\{a,b\}} > 0 \tag{54}$$

for the case of $c > b$. Here the indices $\{a, c\}$ label an excited state of a two-particle system, whereas $\{a, b\}$ label the ground state of such system. In fact, to zero-order approximation we have as a rule

$$E^{(0)}_{\{a,c\}} - E^{(0)}_{\{a,b\}} > 0 \tag{55}$$

for $c > b$. The situation (55) holds for an arbitrary L, whereas our point is that for low excited states in Eq. (54) this situation should be limited to a certain interval of a rather small L.

For a bound electron system, say a hydrogen atom, the kinetic energy T_n of such system increases with decreasing index n of the quantum level because of a stronger limitation of the space occupied by the electron at lower n, hence

$$\Delta T_{n'n} = T_{n'} - T_n < 0 \tag{56}$$

for $n' > n$. On the other hand, for the total energy E we have

$$E_n = -\frac{e^2}{2a_0} n^{-2}, \qquad E_{n'} = -\frac{e^2}{2a_0} n'^{-2}, \tag{57}$$

where a_0 is the Bohr radius, so the total energy change is

$$\Delta E_{n'n} = E_{n'} - E_n > 0 \tag{58}$$

for $n' > n$. Hence the sign of $\Delta T_{n'n}$ [see Eq. (56)] is opposite to that of $\Delta E_{n'n}$ in Eq. (58). Assuming that such situation is typical for a bound system we seek, in our model, such parameter $L = L_c$ which makes the sign of ΔE given in Eq. (54) opposite to the sign of

$$\Delta T = \Delta E^{(0)} \tag{59}$$

where $\Delta E^{(0)}$ is the expression represented in Eq. (55).

In Table 4 we show the L_c calculated for several states $\{a, c\}$ and $\{a, b\}$ for which $c > b$.

7 Dipole transitions and the lifetime of the excited states in a one-dimensional system

Let us assume that an electron is promoted from the level N to some level $N + A$. There exists certain probability of a spontaneous transition back from $N + A$ to N. The transition is accompanied by an emission of a quantum of energy

$$\hbar\omega_{N+A,N} = E_{N+A} - E_N. \tag{60}$$

In Sect. 3 we presented the way of calculating the effect of the electron correlations upon $\hbar\omega_{N+A,N}$. The natural breadth Γ of the emitted line, or its reciprocal value $1/\Gamma$ equal to the lifetime of the excited state, can be calculated from the relation [115]:

$$\Gamma = \frac{4}{3}\omega^3_{N+A,N}\frac{e^2}{\hbar c^3}\left|\left\langle N + A\left|\sum_{i=1}^{N} z_i\right|N\right\rangle\right|^2 = \frac{4}{3}\omega^3_{N+A,N}\frac{e^2}{\hbar c^3}|\langle\varphi_{N+A}|z|\varphi_N\rangle|^2, \tag{61}$$

where φ_{N+A} and φ_N are one-electron wave functions; for the last step in Eq. (61) see Eq. (65) below. Usually the Pauli correlated, but Coulomb uncorrelated wave functions of the kind represented in Eq. (61) are applied in the calculation of Γ because of an enormous difficulty of the calculation of their correlated

Table 4. Box lengths L_c and L_{cc} giving the metal-insulator transition for the excited 2, 3 and 4-particle systems

e.s.	L_c	L_{cc}
Two-particle systems; ground state: $\{1,2\}$		
$\{1,3\}$	6.42×10^{-7}	5.55×10^{-7}
$\{1,4\}$	5.62×10^{-6}	4.73×10^{-6}
Three-particle systems; ground state: $\{1,2,3\}$		
$\{1,2,4\}$	4.32×10^{-7}	4.07×10^{-7}
$\{1,2,5\}$	6.46×10^{-7}	6.11×10^{-7}
$\{1,2,6\}$	1.31×10^{-6}	1.23×10^{-6}
$\{1,2,7\}$	2.96×10^{-6}	2.78×10^{-6}
$\{1,3,5\}$	1.84×10^{-6}	1.60×10^{-6}
$\{1,3,6\}$	2.24×10^{-6}	2.00×10^{-6}
$\{1,3,7\}$	1.58×10^{-5}	1.39×10^{-6}
Four-particle systems; ground state: $\{1,2,3,4\}$		
$\{1,2,3,5\}$	3.56×10^{-7}	3.44×10^{-7}
$\{1,2,3,6\}$	4.90×10^{-7}	4.74×10^{-7}
$\{1,2,3,10\}$	1.95×10^{-6}	1.88×10^{-6}
$\{1,2,4,5\}$	5.47×10^{-7}	5.13×10^{-6}
$\{1,2,4,6\}$	5.47×10^{-7}	5.20×10^{-6}
$\{1,2,4,10\}$	1.40×10^{-6}	1.34×10^{-6}
$\{1,2,5,6\}$	8.20×10^{-7}	7.69×10^{-7}
$\{1,2,5,10\}$	1.51×10^{-6}	1.43×10^{-6}
$\{1,2,6,7\}$	1.51×10^{-6}	1.41×10^{-6}
$\{1,2,6,10\}$	1.98×10^{-6}	1.88×10^{-6}
$\{1,2,7,8\}$	3.07×10^{-6}	2.86×10^{-6}
$\{1,2,7,10\}$	2.37×10^{-6}	2.24×10^{-6}
$\{1,3,4,6\}$	9.51×10^{-6}	8.05×10^{-6}
$\{1,3,4,8\}$	1.80×10^{-5}	1.60×10^{-5}
$\{1,3,5,7\}$	2.15×10^{-6}	1.92×10^{-6}
$\{1,3,5,9\}$	4.53×10^{-6}	4.09×10^{-6}
$\{1,3,7,9\}$	2.25×10^{-5}	2.01×10^{-5}
$\{1,3,7,10\}$	2.82×10^{-5}	2.54×10^{-5}

e.s. means the excited state; L_c is for a Coulomb-correlated system, L_{cc} is for a Coulomb-and-core correlated system; see Sect. 6. The ground state is $\{1, 2\}$, $\{1, 2, 3\}$ and $\{1, 2, 3, 4\}$, respectively, for 2-, 3- and 4-particle system. Numbers in the curly brackets label the occupied orbitals

counterparts. In the case of our one-dimensional gas we can ovecome this difficulty by calculating

$$|N^{\mathrm{corr}}\rangle \approx |N\rangle + \sum_{|M\rangle}\sum_{a}\sum_{c}\left[\left\langle ac\left|\frac{e^2}{r_{12}}\right|Mc\right\rangle - \left\langle ac\left|\frac{e^2}{r_{12}}\right|cM\right\rangle\right] \times\left[\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2}(N^2-M^2)\right]^{-1}|M\rangle$$

$$+\frac{1}{4}\sum_a\sum_b\sum_c\sum_d\left[\left\langle ab\left|\frac{e^2}{r_{12}}\right|cd\right\rangle-\left\langle ab\left|\frac{e^2}{r_{12}}\right|dc\right\rangle\right]$$

$$\times\left[\frac{\hbar^2}{2m_e}\frac{\pi^2}{L^2}(a^2+b^2-c^2-d^2)\right]^{-1}|c,d\rangle$$

$$\equiv|N\rangle+\sum_{|M\rangle}C^{(M)}(N)|M\rangle+\sum_{|c,d\rangle}C^{(c,d)}(N)|c,d\rangle \tag{62}$$

which is the correlated ground-state; $a, c = 1, 2, \ldots, N$; $c \neq a$ in the first sum while $|M\rangle$ are the antisymmetrized one-electron excited ($a \rightarrow M$) wave functions, $M = N + 1; N + 2, \ldots$. In the second sum $|c, d\rangle$ are the antisymmetrized two-electron-excited wave functions obtained by promoting two electrons from levels a, b to levels c, d, correspondingly; $a, b = 1, 2, \ldots, N, a \neq b$ and $c, d = N + 1, N + 2, \ldots, c \neq d$. In a similar way we have

$$|(N+A)^{\text{corr}}\rangle\approx|N+A\rangle+\sum_M C^{(M)}(N+A)|M\rangle+\sum_{|c,d\rangle}C^{(c,d)}(N+A)|c,d\rangle \tag{63}$$

which is the excited Coulomb correlated state. The coefficients $C^{(M)}(N+A)$ in the first sum in Eq. (63) are those given in Eq. (62) on condition that N is replaced by $N+A$ and $a, c = 1, 2, \ldots, N-1, N+A, c \neq a$ and $M = N, N+1, \ldots, M \neq N+A$; also $C^{(c,d)}(N+A)$ in the second sum in Eq. (63) are those given in Eq. (62) on condition that $a, b = 1, 2, \ldots, N-1, N+A, a \neq b$ and $c, d = N, N+1, \ldots, c, d \neq N+A, c \neq d$.

In the correlated case we calculate Γ similarly as in Eq. (61):

$$\Gamma=\frac{4}{3}(\omega_{N+A,N}^{\text{corr}})^3\frac{e^2}{\hbar c^3}\left|\left\langle(N+A)^{\text{corr}}\left|\sum_{i=1}^{N}z_i\right|N^{\text{corr}}\right\rangle\right|^2. \tag{64}$$

Both the wave functions $|N^{\text{corr}}\rangle$ and $|N+A^{\text{corr}}\rangle$ are expressed in Eq. (62) and (63), correspondingly, in the form of linear combinations of Slater determinants $|P\rangle$. When calculating $\langle N+A^{\text{corr}}|\sum_{i=1}^{N}z_i|N^{\text{corr}}\rangle$ we take into account that the matrix element $\langle P'|\sum_{i=1}^{N}z_i|P\rangle$ of the single-particle operator $z=\sum_{i=1}^{N}z_i$ between a Slater determinant $|P\rangle$ entering Eq. (62) and another Slater determinant $|P'\rangle$ present in Eq. (63) can be non-zero only if $|P\rangle$ and $|P'\rangle$ are identical or if $|P\rangle$ differs from $|P'\rangle$ in the occupation of only one level. In the latter case we obtain

$$\left\langle P'\left|\sum_{i=1}^{N}z_i\right|P\right\rangle=\langle\varphi_i|z|\varphi_j\rangle, \tag{65}$$

where the different one-electron orbital is φ_j for $|P\rangle$ and φ_i for $|P'\rangle$. Thus, in the zeroth order, i.e. for the uncorrelated wave functions $|N\rangle$, $|N+A\rangle$, we obtain the term $\langle\varphi_{N+A}|z|\varphi_N\rangle$ present in Eq. (61). For the correlated wave functions $|N^{\text{corr}}\rangle$, $|N+A^{\text{corr}}\rangle$ this term is amended by other terms coming from the correlation parts of $|N^{\text{corr}}\rangle$ and $|N+A^{\text{corr}}\rangle$ present in Eqs. (62) and (63).

An interesting point here is a comparison of the transition probabilities between the uncorrelated, viz., one-electron ground and excited states, on the one hand, and transition probabilities between the correlated two-electron ground and excited states representing an electron pair, on the other hand.

For the uncorrelated wave functions only some special transitions between the one-electron states do not vanish. Let us take, for example, a two-particle system occupying, respectively, two levels a, b and two levels c, d. For the states $\{a, b\}$ and $\{c, d\}$, represented by the Coulomb uncorrelated wave functions $\psi^{(0)}\{a, b\}$ and $\psi^{(0)}\{c, d\}$ [cf. Eq. (47a)], the dipole matrix element between these wave functions has the property

$$\langle \psi^{(0)}\{a, b\} | z_1 + z_2 | \psi^{(0)}\{c, d\} \rangle \neq 0 \tag{66}$$

only in case when at least one of the relations

$$a = c, \quad a = d, \quad b = c, \quad b = d \tag{67}$$

is satisfied; see Eq. (70) below. Otherwise a vanishing transition probability between the states $\{a, b\}$ and $\{c, d\}$ of the particle pair is obtained. On the other hand, the Coulomb correlated wave functions $\psi\{a, b\}$ and $\psi\{c, d\}$ can combine, in principle, into a non-zero matrix element

$$\langle \psi\{a, b\} | z_1 + z_2 | \psi\{c, d\} \rangle \tag{68}$$

for any a, b, c and d. In our opinion this property has not been yet examined thoroughly enough even for so simple and well-known two-electron systems as the He atom, or the H_2 molecule, where the probabilities for only one-electron transitions have been examined [107, 119–122]. The reason for that can be ascribed to a complicated calculation connected with the correlated wave functions of any two-electron (and more than two-electron) excited state.

Let us assume in our model that the electron pair is first on the levels A, B and next the same pair is promoted to the levels C, D, where $A \neq B \neq C \neq D$. In case when the Coulomb correlations between electrons in the pair are taken into account, we find that the matrix element for a dipole transition between the two-electron state $\psi\{A, B\}$ to a similar state $\psi\{C, D\}$ is equal to the term

$$\sum_a \sum_b \sum_c \sum_d C^{(a,b)}(A, B)\, C^{(c,d)}(C, D) \langle \psi^{(0)}\{a, b\} | z_1 + z_2 | \psi^{(0)}\{c, d\} \rangle; \tag{69}$$

the sums run over all possible $a \neq b$ and all possible $c \neq d$. In Eq. (69), we have

$$\langle \psi^{(0)}\{a, b\} | z_1 + z_2 | \psi^{(0)}\{c, d\} \rangle$$
$$= \delta_{bd} \langle a|z|c \rangle + \delta_{ac} \langle b|z|d \rangle - \delta_{bc} \langle a|z|d \rangle - \delta_{ad} \langle b|z|c \rangle. \tag{70}$$

In fact, because of correlations, $C^{(a,b)}(A, B)$, $C^{(c,d)}(C, D)$ are usually non-zero for any pair of levels a, b and c, d and this provides us, together with Eq. (70) with the non-vanishing result for Eq. (69). In effect, we can calculate the reciprocal lifetime Γ of a correlated excited state having the non-vanishing dipole transition to the correlated ground state from the formula (64).

In Table 5 we present dipole moments calculated for several sets of states with the aid of the correlated and uncorrelated wave functions for 2-particle and 5-particle systems; different box length L is taken into account. Table 6 represents the reciprocal lifetimes Γ for the excited states of these systems calculated with the aid of Eq. (61) or Eq. (64), in dependence on the approximations applied for the wave functions and their energies.

Table 5. Dipole moments (in 10^{-2} m) for two-particle and five-particle systems calculated with the aid of the Coulomb uncorrelated and Coulomb correlated wave functions for different L given in 10^{-10} m

State	$L = 1$	$L = 10$
Two-particle systems		
$\{1, 3\}$	-2.07×10^{-9}	-1.98×10^{-8}
	-1.95×10^{-9}	-1.95×10^{-8}
$\{2, 6\}$	-3.53×10^{-11}	1.61×10^{-9}
	-3.97×10^{-11}	-3.97×10^{-10}
$\{5, 7\}$	1.23×10^{-13}	-8.87×10^{-10}
	0.00	0.00
Five-particle system		
$\{1, 2, 3, 4, 6\}$	-2.22×10^{-9}	-2.88×10^{-8}
	-2.01×10^{-9}	-2.01×10^{-8}
$\{1, 2, 3, 4, 15\}$	0.00	0.00
	0.00	0.00
$\{1, 2, 3, 4, 20\}$	-6.30×10^{-12}	-6.91×10^{-11}
	-5.76×10^{-12}	-5.76×10^{-11}

For two-particle systems the moments are between the ground state $\{1, 2\}$ and that indicated in the table; for five-particle systems the moments are between the ground state $\{1, 2, 3, 4, 5\}$ and that indicated in the table. Numbers in the curly brackets label the occupied orbitals. Upper row for each state: correlated dipole moments; lower row – uncorrelated dipole moments. The dipole moments for transitions of two-particle system from the following low-lying excited states not indicated in the table, viz., $\{1, 4\}, \{1, 6\}, \{2, 3\}, \{2, 5\}, \{3, 4\}, \{3, 6\}, \{4, 5\}, \{5, 6\}$, to the ground state $\{1, 2\}$, are equal to zero in the correlated and uncorrelated approximation for the wave functions

8 Two-photon emission and the lifetime of the uncorrelated and correlated excited states in case of forbidden dipole transitions

When a dipole transition between two states of a two-particle system, say $\{a, c\}$ and $\{a, b\}$, is forbidden (a, b, c represent the occupied levels in each case), viz.

$$\langle\{a, c\}|z_1 + z_2|\{a, b\}\rangle = 0, \tag{71}$$

there is a possibility of a two-photon transition between $\{a, c\}$ and $\{a, b\}$ via an intermediate state $\{f, g\}$ [123–129]. Let us assume, for example, that

$$E_{\{a,c\}} > E_{\{a,b\}}. \tag{72}$$

Then a particle promoted into some state $\{f, g\}$ for which

$$E_{\{f,g\}} > E_{\{a,c\}} \tag{73}$$

and

$$\langle\{a, c\}|z_1 + z_2|\{f, g\}\rangle \neq 0 \tag{74}$$

Table 6. Reciprocal lifetime Γ (in s^{-1}) of excited states of two-particle and five-particle systems having different L calculated for the spontaneous dipole transitions; Eqs. (61) and (64)

State	$L = 1$	$L = 10$
Two-particle systems		
$\{1, 3\}$	1.26×10^{12}	2.88×10^{8}
	1.12×10^{12}	3.44×10^{8}
	9.55×10^{11}	9.55×10^{7}
$\{2, 6\}$	1.15×10^{11}	4.27×10^{8}
	1.45×10^{11}	2.37×10^{7}
	1.36×10^{11}	1.36×10^{7}
$\{5, 7\}$	1.03×10^{7}	7.23×10^{8}
	0.00	0.00
	0.00	0.00
Five-particle systems		
$\{1, 2, 3, 4, 6\}$	1.57×10^{13}	5.74×10^{9}
	1.29×10^{13}	4.39×10^{9}
	1.08×10^{13}	1.08×10^{9}
$\{1, 2, 3, 4, 15\}$	0.00	0.00
	0.00	0.00
	0.00	0.00
$\{1, 2, 3, 4, 20\}$	4.38×10^{12}	7.21×10^{8}
	3.54×10^{12}	3.54×10^{8}
	3.67×10^{12}	5.00×10^{8}

The transitions are: (i) between an excited state $\{a, b\}$ indicated in the table and state $\{1, 2\}$ which is the ground state for 2-particle system, and (ii) an excited state $\{a, b, c, d, e\}$ given in the table and state $\{1, 2, 3, 4, 5\}$ which is the ground state for 5-particle system; numbers in the curly brackets label the occupied orbitals; L are given in 10^{-10} m units. Upper row: reciprocal lifetime for transitions between the Coulomb correlated states; middle row: reciprocal lifetime for transitions between the Coulomb uncorrelated (Hartree–Fock) states; lower row: reciprocal lifetime for transitions between Coulomb uncorrelated states calculated in zero-order approximation for energy. (The change of sign obtained for transitions between correlated states is the effect of reversal of the energy levels sequence due to correlations; see Sect. 6.)

can be transferred to the level $\{a, b\}$ on condition that

$$\langle \{f, g\} | z_1 + z_2 | \{a, b\} \rangle \neq 0. \tag{74a}$$

In this case we have a two-photon transition between $\{a, c\}$ and $\{a, b\}$. Here $\{a, c\}$ and $\{a, b\}$ can represent either the Pauli correlated (Coulomb uncorrelated), of the Coulomb correlated wave functions.

The probability per second for the simultaneous emission of two photons with one photon in the frequency range $d\nu'$ is [124]

$$A\,d\nu' = \frac{1024\pi^6 e^4 \nu'^3 \nu''^3}{h^2 c^6}\,d\nu' \times \left| \sum_{\{f,g\}} \langle\{a,c\}|z_1 + z_2|\{f,g\}\rangle\langle\{f,g\}|z_1 + z_2|\{a,b\}\rangle \times \left(\frac{1}{\nu_{\{f,g\}\{a,c\}} + \nu''} + \frac{1}{\nu_{\{f,g\}\{a,c\}} + \nu'}\right)\right|^2 . \tag{75}$$

The frequency ν'' is that of the second photon emitted simultaneously with the photon having frequency ν'. In our calculations we limit, on the first step, the sum over $\{f, g\}$ to a single intermediate state in each case, on the next step we perform a sum over $\{f, g\}$. The principle of the conservation of energy requires that

$$\nu' + \nu'' = \nu_{\{a,c\}\{a,b\}} = \frac{E_{\{a,c\}} - E_{\{a,b\}}}{h}, \tag{76}$$

whereas

$$\nu_{\{f,g\}\{a,c\}} = \frac{E_{\{f,g\}} - E_{\{a,c\}}}{h}. \tag{77}$$

The formula (75) can be used for the probability of simultaneous emission of a pair of photons with no distinction concerning the order of emission. The total probability of emission equal to the reciprocal value of the lifetime of the higher level is thus [124]

$$w = \frac{1}{2}\int_0^{\nu_{\{a,c\}\{a,b\}}} A\,d\nu'. \tag{78}$$

In Table 7 we present the reciprocal lifetime for a set of states having forbidden dipole transitions but the transitions between the states can be effectuated via two-photon transitions. The calculations are done for $L = 10^{-9}$ m; an increase of L leads to a strong decrease of the reciprocal lifetime w for a two-photon transition between given states.

9 Average velocity of an uncorrelated and correlated pair of free particles

In the low-temperature physics we examine the problem of the coherence length ξ_0 in a many-electron system which can be defined as the ratio between the electron velocity v_F at the Fermi level and the size E_g of the energy gap of a metallic superconductor [130]:

$$\xi_0 = v_F/\pi E_g. \tag{79}$$

Our point is that v_F should evidently depend on the Coulomb correlations in the system and we examine this correlation effect on the particle velocity in our model. For a one-dimensional two-particle system the velocity operator is

$$\hat{v}_{\text{pair}} = \frac{\hbar}{i m_e}\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right). \tag{80}$$

Table 7. Correlation influence on probability w of two-photon transition from state $\{c, d\}$ to state $\{a, b\}$ in case of a forbidden dipole transition between these states; see Sect. 8

Intermediate state	$\Delta E^{(0)}$	$w^{(0)}$	$\Delta E^{(\mathrm{HF})}$	$w^{(\mathrm{HF})}$	$\Delta E^{(\mathrm{HFcorr})}$	$w^{(\mathrm{HFcorr})}$
Forbidden dipole transition $\{1,4\} \to \{1,2\}$						
$\{2,4\}$	1.13	4.88×10^{-2}	5.59×10^{-1}	5.16×10^{-1}	8.57×10^{-1}	5.49×10
$\{1,5\}$	3.38	3.26×10^{-2}	4.00	2.39×10^{-1}	4.13	1.44×10^{-1}
$\{1,7\}$	1.24×10	4.71×10^{-6}	1.40×10	4.07×10^{-5}	6.72	1.20×10^{-2}
$\{1,9\}$	2.44×10	3.00×10^{-8}	2.68×10	2.83×10^{-7}	9.89	6.12×10^{-3}
$\{1,11\}$	3.95×10	7.54×10^{-10}	4.24×10	7.51×10^{-9}	1.39×10	3.58×10^{-3}
		1.63×10^{-1}		1.47		6.45×10
Forbidden dipole transition $\{2,3\} \to \{1,2\}$						
$\{2,4\}$	2.63	2.13×10^{-3}	3.43	4.36×10^{-3}	3.05	8.31×10^{-1}
$\{2,6\}$	1.02×10	2.02×10^{-7}	1.23×10	4.51×10^{-7}	6.50	8.90×10^{-5}
$\{2,8\}$	2.07×10	9.71×10^{-10}	2.37×10	2.40×10^{-9}	8.92	5.56×10^{-3}
$\{2,10\}$	3.42×10	2.00×10^{-11}	3.79×10	5.27×10^{-11}	1.21×10	1.45×10^{-5}
$\{2,12\}$	5.08×10	9.19×10^{-13}	5.50×10	2.53×10^{-12}	1.61×10	4.55×10^{-5}
		2.18×10^{-3}		4.45×10^{-3}		7.21×10^{-1}
Forbidden dipole transition $\{3,4\} \to \{1,2\}$						
$\{1,5\}$	—	0	—	0	1.27	1.67×10^{-2}
$\{3,5\}$	—	0	—	0	3.68	5.28
$\{2,6\}$	—	0	—	0	6.85	6.61×10^{-3}
$\{4,6\}$	—	0	—	0	1.09×10	2.88×10^{-1}
$\{1,7\}$	—	0	—	0	1.17×10	4.68×10^{-5}
		0		0		8.26

First column: symbol of the intermediate state $\{e,f\}$. Next columns: energy difference ΔE between states $\{e,f\}$ and $\{c,d\}$ (in eV) and the reciprocal lifetime w (in s^{-1}) calculated for different approximations (zero-order, Hartree–Fock, and Hartree–Fock with the second-order perturbation correction for energy and obtained with the aid of the Coulomb-correlated wave functions). In case (iii) also two-photon transitions are forbidden for the uncorrelated (zero-order and Hartree–Fock) wave functions; $L = 10^{-9}$ m. The bottom numbers for w represent results when the sum over the intermediate states $\{f, g\}$ is taken into account in (75)

The average of $\hat{v}_{\mathrm{pair}}$ calculated over any wave function vanishes because of the standing-like character to the wave functions in our model, nevertheless we can examine the average value of

$$\hat{v}^2_{\mathrm{pair}} = -\frac{\hbar^2}{m_e^2}\left(\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2} + 2\frac{\partial^2}{\partial z_1 \partial z_2}\right). \tag{81}$$

For the case of an uncorrelated wave function the average of the last operator term entering Eq. (81) vanishes leading to a well-known result proportional to the kinetic energy of the system equal to a sum of kinetic energies of individual particles, viz.,

$$\frac{1}{2} m_e \langle \hat{v}^2_{\mathrm{pair}} \rangle = -\frac{\hbar^2}{2m_e}\left\langle \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2} \right\rangle = E_{\mathrm{kin}}. \tag{82}$$

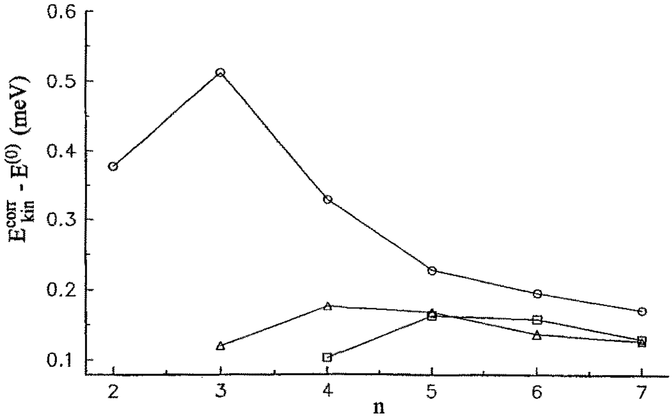

Fig. 10. The difference (in meV) between the Coulomb correlated and Coulomb uncorrelated kinetic energy, viz. $E^{\text{corr}}_{\text{kin}} - E^{(0)}$, of a 2-particle system as a function of the system excitations. System states are represented by $\{m, n\}$ where m, n label the occupied levels. Circles: $m = 1, n = 2, 3, 4, 5, 6, 7$; triangles: $m = 2$; $n = 3, 4, 5, 6, 7$; squares: $m = 3, n = 4, 5, 6, 7$. $L = 10^{-7}$ m

In case of the uncorrelated wave function the average in Eq. (82) gives $E^{(0)}$, which is the kinetic energy of the uncorrelated two-particle system.

In Fig. 10 we plot the difference of the average of Eq. (82) calculated for the Coulomb correlated $\psi\{m, n\}$ and the Coulomb uncorrelated (Pauli correlated) $\psi^{(0)}\{m, n\}$, respectively, for different m and n.

Two points are still of interest. The first concerns the behavior of the average of the operator (81) as a function of L for a given state of the particle pair calculated in the case of: (i) the correlated wave function, and (ii) the uncorrelated wave function of the pair. In case (ii) this average is reduced to that obtained for the operator entering Eq. (82),

$$\langle \hat{v}^2_{\text{pair}} \rangle = \frac{2E^{(0)}}{m_e}. \qquad \text{(82a)}$$

The averages of Eq. (81) decrease monotonically with the increase of L, nevertheless their ratio

$$\langle \psi\{m, n\} | \hat{v}^2_{\text{pair}} | \psi\{m, n\} \rangle / \langle \psi^{(0)}\{m, n\} | \hat{v}^2_{\text{pair}} | \psi^{(0)}\{m, n\} \rangle \qquad \text{(83)}$$

exhibits an evident maximum for a high-excited state; see Fig. 11. These maxima calculated for the states $\psi\{1, 2\}, \psi\{1, 3\}$ and $\psi\{1, 4\}$ are attained at L not far from L_c characteristic for the metal–insulator transition of a two-particle system; see Sect. 6. Another point of interest is the examination of the difference of the averages represented by the Coulomb correlated average of Eq. (81) and the average given in Eq. (82a) for different excitations of the particle pair; see Fig. 12. Expressions (81) and (82a) taken separately increase monotonically with the excitation index of the state, but their difference exhibits oscillations; Fig. 12. Maxima similar to those shown in Fig. 12 can be observed also for the ratio (83) when it is plotted for some constant $m > 1$ and increasing n.

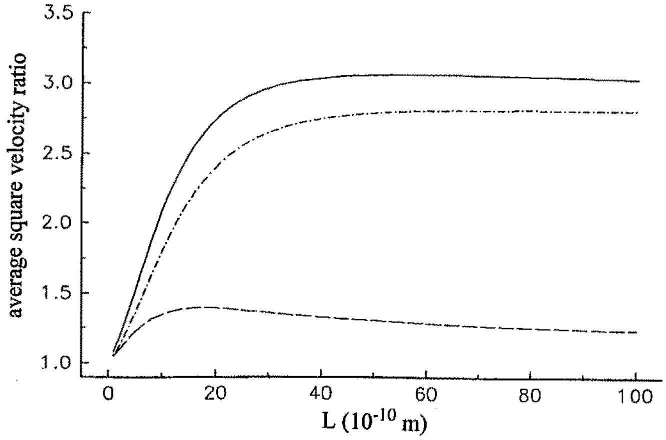

Fig. 11. The ratio of the average square of the Coulomb correlated and Coulomb uncorrelated velocity represented in Eq. (83) and calculated as a function of L (in 10^{-10} m) for different states of a two-particle system. Upper curve: state $\{1, 2\}$; middle curve – state $\{1, 3\}$, lowest curve – state $\{1, 4\}$

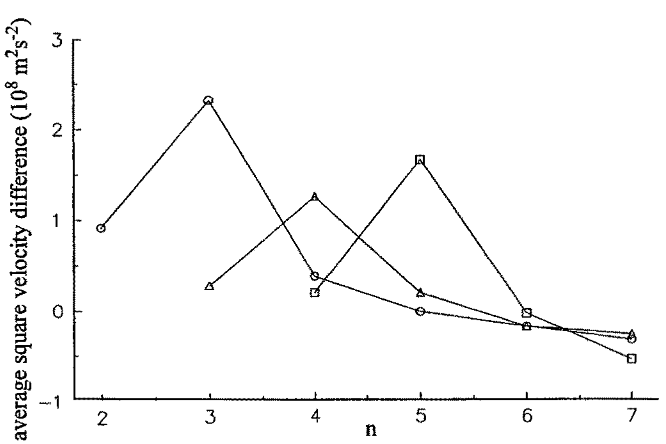

Fig. 12. The difference in the average square of the Coulomb correlated and Coulomb uncorrelated velocity of a two-particle system, viz. $\langle\psi\{m, n\}|\hat{v}^2_{\text{pair}}|\psi\{m, n\}\rangle - \langle\psi^{(0)}\{m, n\}|\hat{v}^2_{\text{pair}}|\psi^{(0)}\{m, n\}\rangle$ (in 10^8 m^2 s^{-2}), represented as a function of the system excitations. System states are $\{m, n\}$, where m, n label the occupied levels. Circles: $m = 1, n = 2, 3, 4, 5, 6, 7$; triangles: $m = 2$; $n = 3, 4, 5, 6, 7$; squares: $m = 3, n = 4, 5, 6, 7, L = 10^{-7}$ m

10 Survey

A well-known one-dimensional problem of interacting electric charges moving in a very thin potential tube has been approached on the basis of a standard quantum-mechanical perturbation theory. The charged particles are assumed to be electrons which may occupy, however, only singly their one-particle quantum levels. A full convergence of the perturbation calculation performed for the Coulomb operator is then attained because the terms which depend on the cross-section radius R of the potential box can be easily separated from the perturbation terms independent of R on condition that R is taken sufficiently small. The R-dependent terms cancel in the calculation of the excitation energies.

The numerical calculations are done to the second-order approximation for energy which is assumed to give an important contribution to the correlation energy; nevertheless high-order terms have been also included in order to compare the accuracy of the Rayleigh–Schrödinger perturbation energies with similar energies obtained using shifted-energy denominators.

The applications of the theory were focussed on four kinds of problems. The first concerned the excitation energies of the model particles and their dependence on the potential box length L. Here we examined the L for which the zero-order excitation spectrum characteristic for a one-dimensional metal can be changed into a spectrum characteristic for a bound, or insulating, few-electron system.

In the second step, we examined the effect of the Coulomb repulsion on the charge distribution in small systems. Here the influence of the particle excitations done in the upper levels on the charge distribution obtained in the bottom levels can be also examined. The patterns of the correlated and uncorrelated charge density of a two-particle system being in different energy states are thoroughly compared.

The third kind of problems concerned the calculation of electric dipole moments and their application to transition probabilities between different states. Some transitions which are forbidden for the states represented with the aid of the uncorrelated wave functions become allowed in the case when the Coulomb-correlated wave functions are used in calculations. Also probabilities obtained for two-photon transitions between the states are compared for different approximations applied in the perturbation theory.

The problems of the fourth kind concerned the velocity square of a correlated two-particle system. In the case of an uncorrelated system its velocity square becomes equivalent, with the accuracy to a constant factor, to the kinetic energy of that system. This situation is changed, however, when the correlated wave functions are taken into account and our purpose was to examine the changes in the velocity behavior due to correlations.

All calculations were done on the basis of the fundamental constants $e, m_e, \hbar$ characterizing the electron particles and their levels together with the length L of the one-dimensional potential box as the only variable parameter in the model.

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