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Coulomb Interaction in the One-Dimensional Free-Electron Model

P. JOHN ROBERTS

Mathematics Department, University Institute of Science and Technology, Manchester 1, England

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In the limiting case of the free-electron theory where the electron motion is constricted to one dimension, the one-dimensional Coulomb potential gives rise to divergent interaction integrals. It is shown that a proposal by Olszewski to remove the divergenses by first evaluating the integrals in the three-dimensional case and then passing to the limit of one dimension only is incorrect, and that convergent integrals may only be obtained by suitably modifying the original one-dimensional Coulomb potential between particles.

In dem Grenzfall des Modells der „Freien Elektronen", in dem die Elektronenbewegung auf eine Dimension eingeschränkt ist, ergibt das eindimensionale Coulombpotential divergente Wechselwirkungsintegrale. Es wird gezeigt, daß ein Vorschlag von Olszewski zur Aufhebung der Divergenz durch Übergang von dreidimensionalen zum eindimensionalen Integral falsch ist. Konvergente Integrale können nur durch geeignete Veränderung des ursprünglichen eindimensionalen Coulombpotentials erhalten werden.

Dans le cas limite de la théorie de l'électron libre à une dimension, le potentiel coulombien donne lieu à des intégrales d'interaction divergentes. On montre que la proposition d'Oszewski pour éliminer les divergences, en évaluant d'abord les intégrales tridimensionnelles et en passant à la limite à une dimension, est incorrecte et que des intégrales convergentes ne peuvent être obtenues qu'en modifiant le potentiel coulombien unidimensionnel entre particules.

Introduction

Although the one-dimensional free-electron (FE) model for conjugated molecules offers a way of avoiding the mathematical pitfalls which more rigorous treatments of the Schrödinger equation encounter, it is well known [1] that the one-dimensional limit $|x_1 - x_2|^{-1}$ of the Coulomb three-dimensional potential r_{12}^{-1} between electrons 1 and 2 gives rise to divergent integrals if we try to calculate the Coulomb interaction energy between pairs of electrons when the latter are described by one-dimensional potential box wavefunctions. One way of avoiding this difficulty for two electrons only confined between infinite potential barriers and constrained to move in one dimension is to solve the one-dimensional free-electron Schrödinger equation with the Coulomb interaction $|x_1 - x_2|^{-1}$ between the electrons [2]. Because of the boundary conditions at the walls of the potential box, the problem of ascertaining the eigen-values in this case is best performed numerically.

The occurrence of these infinities is a long-standing result from classical physics, where it is known that the mutual electrostatic energy of two two-dimensional charge distributions on the same surface is finite, whereas the mutual

electrostatic energy of two one-dimensional charge distributions (cf. self-energy of a line distribution) is logarithmically infinite.

To arrive at a representation of the interaction between two electrons which will bear some relation to the physics of the situation and yet will enable us to calculate interaction integrals without giving rise to divergences, various tricks have been resorted to by those quantum chemists who have wished to include, say, π-σ interactions in the crude FE model. If we denote the distance between two electrons in one dimension by x, then the simplest approximation is to replace the true Coulomb potential function x^{-1} for all x by a cut-off potential

$$\left.\begin{aligned} V(x) &= 1/x\,, \quad x \geqq D\,, \\ &= 0\,, \quad x < D\,, \end{aligned}\right\} \tag{1}$$

or a slight modification

$$\left.\begin{aligned} V(x) &= 1/x\,, \quad x \geqq D\,, \\ &= 1/D\,, \quad x \leqq D\,, \end{aligned}\right\} \tag{2}$$

where D is a cut-off radius, which, for example, might be comparable to the electron diameter. A zero cut-off of type (1) was used by the Japanese group [3], and type (2) was used by the Chicago group [1].

Another way out of the divergence difficulty does just the opposite to this. In the cut-off methods the long-range part of the Coulomb potential is retained, whereas the short-range behaviour is entirely dispensed with, whereas the argument could be made that in any interaction integrals the major contribution from the Coulomb potential comes from its short-range behaviour. Thus this school of thought dispenses with the long-range "tail" to the Coulomb operator and replaces its short-range part by a new potential function which is integrable, namely the Dirac-delta-function:

$$\begin{aligned} V(x) &= g\delta(x)\,, \qquad (3) \\ \delta(x) &= 0\,, \quad x \neq 0\,, \\ \delta(0) &= \infty\,, \\ \int_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x &= 1\,, \\ \int_{-\infty}^{\infty} \delta(x) f(x)\,\mathrm{d}x &= f(0)\,, \end{aligned}$$

where g is the strength of the potential. With this potential, the interaction integrals are greatly simplified, and are convergent, but Ham and Ruedenberg [1] were not encouraged by the results of trial calculations with a delta-function interaction. An extension of this model to molecules in which the electron-nuclear attractions are replaced by δ-functions was carried out by Frost [4]. So far as the author is aware, no calculations on $\pi-\pi$ or $\pi-\sigma$ interactions have been carried out with a combination of (1) and (3), namely

$$\left.\begin{aligned} V(x) &= 1/x\,, \quad x \geqq D \\ &= g\,\delta(x)\,, \quad x < D \end{aligned}\right\} \tag{4}$$

with g as the strength of the δ-function (a suitable choice would be $g = 1$). The potential (4) would enable us to calculate the inter-electronic interaction integrals without divergences, yet allows both the long- and short-range behaviour of the Coulomb potential to be reproduced.

A novel way of avoiding divergences was used by Labhart [5], who expressed the Coulomb and exchange integrals in FEMO theory in terms of an effective distance between the volume elements of the interaction charge distributions, the effective distance being calculated theoretically in dependence of the geometrical distance. In practice this means using a potential

$$V(x) = \frac{1}{(x^2 + a^2)^{\frac{1}{2}}}, \tag{5}$$

where a is chosen on physical considerations. This potential is now non-singular at the origin, and by choosing a as small as possible we may make (5) approximate the true Coulomb potential, to any arbitrary degree of accuracy, everywhere except at the origin. Obviously the addition of a δ-function at the origin might be expected to improve this model.

A fourth type of approximation consists of taking a two-dimensional average of the three-dimensional Coulomb interaction over a transversal region with an area A. This will result in a non-singular one-dimensional potential, a method which has been used by the Japanese group and others [6, 7]. Thus if the electrons are assumed to be enclosed in a very deep potential field of square-well shape so that their motion is predominantly along the axis of a long thin tube of transversal cross-sectional area A, then the effective one-dimensional potential to be used is

$$V(|x_1 - x_2|) = \frac{1}{A^2} \int \mathrm{d}y_1 \int \mathrm{d}y_2 \int \mathrm{d}z_1 \int \mathrm{d}z_2 \, r_{12}^{-1}, \tag{6}$$

where integration extends over the transversal area A of the tube. Thus Araki *et al.* [6] approximately expanded the Coulomb potential as a Fourier series inside a parallelopiped, and then averaged this over the rectangular transversal area, whereas Sternlicht [7] averaged over the circular cross-sectional area of a long thin cylinder.

In the latter case, as an alternative to the method described in Ref. [7] for performing the average, we describe here a simple method. Constraining the π-electrons to move along the z-axis of a long thin cylinder, radius a, and using the usual cylindrical coordinates (σ, z, ϕ), then the well-known expansion of the Green's function in cylindrical coordinates is

$$r_{12}^{-1} = \sum_{m=-\infty}^{\infty} e^{im(\phi_1 - \phi_2)} \int_0^{\infty} \mathrm{d}t \exp(-t|z_1 - z_2|) \, J_m(t\sigma_1) \, J_m(t\sigma_2), \tag{7}$$

where the subscripts 1 and 2 refer to the two electrons involved and J is the Bessel function.

For a cylindrical tube, (6) becomes

$$V(|z_1 - z_2|) = \frac{\int_0^{2\pi} \mathrm{d}\phi_1 \int_0^{2\pi} \mathrm{d}\phi_2 \int_0^{a} \sigma_1 \, \mathrm{d}\sigma_1 \int_0^{a} \sigma_2 \, \mathrm{d}\sigma_2 \, r_{12}^{-1}}{(\pi a^2)^2}, \tag{8}$$

into which we substitute (7), so that we obtain

$$V = (4/a^4) \int_0^\infty \mathrm{d}t \exp(-t|z_1 - z_2|) \left[\int_0^a \mathrm{d}\sigma \, \sigma \, J_0(\sigma t) \right]^2 . \tag{9}$$

The integral involving the Bessel function is easily evaluated [8], with the result

$$V = \frac{4}{a} \int_0^\infty \mathrm{d}t \exp\left(-\frac{t}{a} |z_1 - z_2| \right) [J_1(t)/t]^2 , \tag{10}$$

where we have made a slight change in the integration variable.

An alternative way of writing (10) is [9]

$$V = (2/a\pi) \int_0^\pi \mathrm{d}\Theta (1 + \cos\Theta) \, [(\alpha^2 + 2 - 2\cos\Theta)^{\frac{1}{2}} - \alpha] , \tag{11}$$

where

$$\alpha = |z_1 - z_2|/a ,$$

and the right-hand side is an elliptic integral. This potential is non-singular when the two electrons coalesce on the axis, since it is easily shown [10] that

$$V(0) = \frac{16}{3\pi a} . \tag{12}$$

From either (8) or (11), it is readily shown that when α is large enough to neglect powers of $1/\alpha$ beyond the first, then

$$V \to \frac{1}{|z_1 - z_2|} , \tag{13}$$

i.e., the one-dimensional Coulomb potential. This limit will obviously only occur if the length of the cylindrical box is much greater than the radius a.

In a series of papers, Olszewski [11] has attempted to solve the problem of the one-dimensional divergences in the FEMO model by first considering electron-electron and electron nuclear interaction integrals for electrons moving freely inside a cylindrical box, with a full three-dimensional treatment of the Coulomb potential, and then tending to the limit of zero box radius, so that the original box is eventually shrunk onto the z-axis. By this device he alleged that no divergences show up when the transition to zero box radius is made on the three-dimensional integrals, but unfortunately his mathematical analysis at this point is in error, due to a most unlucky misunderstanding, and exactly the same logarithmic divergences occur as in the straight-forward one-dimensional treatment with a Coulomb potential. It is the purpose of this paper to demonstrate how these divergences occur for interaction integrals between electrons confined to a cylindrical box, as considered by Olszewski [11], when the box radius shrinks to zero.

Mathematical

Following Nikitine and Komoss [12] we consider the solution for free electrons in a cylindrical box of length L, radius a, with a straightened chain of carbon atoms as the z-axis. Assuming the potential inside the box to be zero, rising to infinity

at the surface of the box, the solution has the form

$$\phi_{nl}(r) = (2/L)^{\frac{1}{2}} N_l \sin(n\pi z/L)\, J_l\left(x_l \frac{\sigma}{a}\right) e^{il\phi}, \quad n \quad 1, 2, 3, \ldots \tag{14}$$

where J is the Bessel function, (σ, z, ϕ) are the usual cylindrical coordinates, N is the normalisation factor, and X_l is the first zero of $J_l(x)$, so that

$$J_l(x_l) = 0\,. \tag{15}$$

From the normalisation integral,

$$(N_l)^{-2} = 2\pi \int_0^a \mathrm{d}\sigma\, \sigma \left[J_l\left(x_l \frac{\sigma}{a}\right)\right]^2 \tag{16}$$

$$= \pi a^2 [J_{l+1}(x_l)]^2, \quad a \neq 0\,. \tag{17}$$

Since we wish to ultimately consider the limit

$$a \to 0\,,$$

we shall retain the form (16) rather than (17) throughout the analysis until the limit is taken.

We shall now consider the interelectronic Coulomb interaction integral between electrons 1 and 2, of the type

$$I = \int \mathrm{d}v_1\, \mathrm{d}v_2 |\phi_{nl}(r_1)|^2\, r_{12}^{-1} |\phi_{m\lambda}(r_2)|^2\,, \tag{18}$$

the integration being carried out over the whole volume of the cylinder. Inserting (14) and (7) into (18), and integrating trivially over the angular coordinates, we have

$$I = \left(\frac{4\pi}{L} N_l N_\lambda\right)^2 \int_0^a \sigma_1\, \mathrm{d}\sigma_1\, J_l^2\left(\frac{x_l \sigma_1}{a}\right) \int_0^a \sigma_2\, \mathrm{d}\sigma_2\, J_\lambda^2\left(x_\lambda \frac{\sigma_2}{a}\right) \int_0^L \mathrm{d}z_1 \int_0^L \mathrm{d}z_2$$
$$\times \sin^2\left(\frac{n\pi z_1}{L}\right) \sin^2\left(\frac{m\pi z_2}{L}\right) \int_0^\infty \mathrm{d}t \exp(-t|z_1 - z_2|)\, J_0(\sigma_1 t)\, J_0(\sigma_2 t)\,. \tag{19}$$

Interchanging the order of the t integration with the z_1, z_2 integrations, and completing the latter, we obtain

$$I = \frac{1}{2}\left(\frac{4\pi}{L} N_l N_\lambda\right)^2 \int_0^a \sigma_1\, \mathrm{d}\sigma_1\, J_l^2\left(\frac{x_l \sigma_1}{a}\right) \int_0^a \sigma_2\, \mathrm{d}\sigma_2\, J_\lambda^2\left(x_\lambda \frac{\sigma_2}{a}\right)$$
$$\times \int_0^\infty \mathrm{d}t\, J_0(\sigma_1 t)\, J_0(\sigma_2 t) \left[\frac{L}{t} + \frac{(e^{-Lt} - 1)\, b^2 c^2}{t^2 (t^2 + b^2)\, (t^2 + c^2)}\right], \tag{20}$$

Where

$$b = \frac{2n\pi}{L}, \quad c = \frac{2m\pi}{L}\,.$$

Since we intend to proceed to the limit $a \to 0$, we shall now insert the expression (16) for the normalisation factors into (20), and then take the limit, where we observe that

$$\underset{a\to 0}{Lt} \int_0^a \mathrm{d}x\, x\, F(x) = \underset{a\to 0}{Lt}\, a^2 F(a)\,. \tag{21}$$

Hence, from (16), (20) and (21) we obtain

$$\underset{a\to 0}{Lt}\, I = (2/L^2) \underset{a\to 0}{Lt} \int_0^\infty \mathrm{d}t\, J_0^2(at) \left[\frac{L}{t} + \frac{(e^{-Lt}-1)(bc)^2}{t^2(t^2+b^2)(t^2+c^2)} \right]. \tag{22}$$

If we now interchange the order of the limit and the integration in (22), we have

$$\underset{a\to 0}{Lt}\, I = (2/L^2) \int_0^\infty \mathrm{d}t \left[\frac{(Lt+e^{-Lt}-1)}{t^2} + \frac{(e^{-Lt}-1)}{(c^2-b^2)} \left(\frac{b^2}{c^2+t^2} - \frac{c^2}{b^2+t^2} \right) \right], \tag{23}$$

for $b \neq c$, and

$$\underset{a\to 0}{Lt}\, I = \frac{2}{L^2} \int_0^\infty \mathrm{d}t \left[\frac{(Lt+e^{-Lt}-1)}{t^2} + \frac{(1-e^{-Lt})(t^2+2b^2)}{(t^2+b^2)^2} \right], \tag{24}$$

for $b = c$, with a slight re-arrangement of the integrand in either case. The right-hand side can be shown, by elementary methods, to contain a logarithmic infinity. For example, the first term in the integrand of (23) or (24) can be shown, by integration by parts, to be (after a slight change in the integration variable):

$$\int_0^\infty \frac{\mathrm{d}t}{t^2}(Lt+e^{-Lt}-1) = L \int_0^\infty \frac{\mathrm{d}t}{t}(1-e^{-t}) - L\,, \tag{25}$$

which is logarithmically divergent [13]. Since the rest of the integral in each case is finite, then we see that the Coulomb integral I tends logarithmically to infinity as the box radius shrinks to zero. The same is true for any other interelectronic interaction integrals, in the limit of zero radius, which agrees with the statement of Ham and Ruedenberg [1].

In the same manner it is easily shown that the electron-nuclear attraction integrals for the Coulomb interaction between an electron and a nucleus on the axis of the tube are also divergent. Denoting the cylindrical polar coordinates of nucleus C on the z-axis of the tube by, (0, c, 0), then the distance between an electron at (σ, z, ϕ) and the nucleus C is

$$r_c = [\sigma^2 + (z-c)^2]^{\frac{1}{2}}\,, \tag{26}$$

for which the one-particle analogue of (7) is

$$r_c^{-1} = \int_0^\infty \mathrm{d}t \exp(-t|z-c|)\, J_0(t\sigma)\,, \tag{27}$$

with J a Bessel function as before. Now the only non-vanishing electron-nuclear attraction integrals are of the type

$$K = \int \mathrm{d}v \frac{\phi_{nl}(r)\phi^*_{ml}(r)}{r_c}, \tag{28}$$

integrated over the whole volume of the box. Inserting (14) and (27) into (28), inverting the order of the t and z integrations, and integrating trivially over ϕ, we obtain

$$K = (2\pi N_l^2/L) \int_0^a \mathrm{d}\sigma\, \sigma \left[J_l\left(x_l \frac{\sigma}{a} \right) \right]^2 \int_0^L \mathrm{d}z \int_0^\infty \mathrm{d}t \exp(-t|z-c|)\, J_0(\sigma t) \times (\cos\alpha z - \cos\beta z), \tag{29}$$

where

$$\alpha = (n-m)\,\pi/L,$$
$$\beta = (n+m)\,\pi/L.$$

Hence, substituting (16) into (29) and taking the limit $a \to 0$ as in (21) we find

$$\underset{a\to 0}{Lt}\, K = (1/L) \int_0^L \mathrm{d}z \int_0^\infty \mathrm{d}t \exp(-t|z-c|)\,(\cos\alpha z - \cos\beta z), \tag{30}$$

where we have taken the limit inside the t integration. Thus

$$\begin{aligned} L \underset{a\to 0}{Lt}\, K &= \int_0^L \frac{\mathrm{d}z(\cos\alpha z - \cos\beta z)}{|z-c|} \\ &= \sin\alpha c\, Si(\alpha c) - \cos\alpha c\, Cin(\alpha c) \\ &\quad - \sin\beta c\, Si(\beta c) + \cos\beta c\, Cin(\beta c) \\ &\quad - \sin\alpha c\, Si(\alpha L - \alpha c) - \cos\alpha c\, Cin(\alpha L - \alpha c) \\ &\quad + \sin\beta c\, Si(\beta L - \beta c) + \cos\beta c\, Cin(\beta L - \beta c) \\ &\quad + \cos\alpha c \left[\int_0^{\alpha c} \frac{\mathrm{d}t}{t} + \int_0^{\alpha(L-c)} \frac{\mathrm{d}t}{t} \right] \\ &\quad - \cos\beta c \left[\int_0^{\beta c} \frac{\mathrm{d}t}{t} + \int_0^{\beta(L-c)} \frac{\mathrm{d}t}{t} \right], \end{aligned} \tag{31}$$

where the sine and cosine integrals are [14]:

$$Si(x) = \int_0^x \frac{\sin t}{t}\,\mathrm{d}t,$$
$$Cin(x) = \int_0^x \frac{(1-\cos t)}{t}\,\mathrm{d}t. \tag{32}$$

Now from (29) we see that since n, m are positive integers, β is always positive, but α may be zero. In the latter case, (31) is replaced by a rather simpler formula, but since $\beta \neq \alpha$, in either case the last four terms in (31) give rise to logarithmic divergences, exactly as with the two-electron integrals. Hence, as before, the process of shrinking the cylinder to zero radius after calculating the full three-dimensional integrals will not remove the one-dimensional divergences, as claimed by Olszewski [11]. The only way to avoid divergences is to in some way modify the one-dimensional Coulomb operator, as described above.

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Dr. P. J. Roberts
Department of Mathematics
University Institute of Science and Technology
P. O. Box No. 88, Sackville Street
Manchester 1, England