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Asymptotic relation between eigenvalue sum and chemical potential for electrons moving in bare point-charge potentials in *d* dimensions

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For electrons moving independently in a d-dimensional bare point-charge potential, the Euler equation of density-functional theory in the limit of large numbers of electrons, N, is combined with the virial theorem to relate the sum of eigenvalues E to the chemical potential μ. The result is $E/N\mu=d(4-d)/(4+2d-d^2)\equiv\alpha^{-1}$. This result (I) is verified by direct calculation of both E and μ for $d=1$, 2, and 3 in the asymptotic limit of large N. Neither does there seem to be any difficulty in applying (I) for $d\geq 5$. But evidently $E/N\mu=0$ for $d=4$; an immediate consequence of the virial theorem for this dimensionality. Viewed as a continuous function of d, $E/N\mu$ is singular at $d=1+\sqrt{5}$ and is negative for $1+\sqrt{5}<d<4$. Excluding this pathological regime of d, it can be shown from (I) that, for a point charge Ze, $E=F(Z,d)N^{\alpha}$, where the exponent α is given by (I).

I. INTRODUCTION

It has been shown in Ref. 1 that for heavy positive ions with nuclear charge Ze and a large number of electrons ($N\leq Z$), the chemical potential μ of the density-functional theory[2] can be used to characterize the total energy E. In subsequent work, following this study of atomic ions which clearly correspond to dimensionality $d=3$, Pucci and the writer have also studied the relation between E and μ in linear polyacenes where it seems plausible that the π electrons will behave more like a two-dimensional assembly. Indeed, by using different approximations to the π-electronic structure, e.g., Hückel theory[3] and alternant molecular orbital theory,[4] these workers have argued that as the number of rings in the polyacenes tends to infinity, the ratio $E/N\mu$ is dominated by the dimensionality, the ratio approaching values quite near to, but not exactly 2^{-1}, the free-electron-gas value in two dimensions.

Therefore, it is of obvious interest to study the ratio $E/N\mu$, with N electrons, for a class of potentials in which the dimensionality d can be varied, since the only other case where we have precise quantitative results is that referred to above, namely the free-electron gas in d dimensions.

Because the positive-ion problem discussed in the present context in Ref. 1 is intimately related to the bare Coulomb field problem, we have chosen to study the class of bare point-charge potentials in d dimensions. Thus, we treat N electrons which move independently in bare potentials generated by a charge Ze in d dimensions. Even with this problem, it is only for the Coulomb case, $d=3$, that we can obtain exact results for the eigenvalue sum E when the N electrons doubly occupy the lowest available energy levels with spin degeneracy in accord with the Pauli exclusion principle. However, we shall demonstrate below that, in the asymptotic limit in which N and Z are large, the ratio $E/N\mu$ can be calculated explicitly as a function of dimensionality d.

II. POTENTIALS OF BARE CHARGE *Ze* IN *d* DIMENSIONS

In d dimensions we are concerned with potentials $\phi_d(r)$ obeying the Poisson equation

$$\nabla_d^2\phi(r)=-4\pi Ze\delta(r)\ . \tag{2.1}$$

This has solution, as discussed, for example by Kventsel and Katriel,[5]

$$\begin{aligned}\phi_d(r)&=\frac{4\pi Ze\Gamma(d/2+1)}{d(d-2)\pi^{d/2}}r^{2-d}\ ,\quad d\geq 3\\ \phi_2(r)&=-2Ze\ln r\ ,\quad d=2\\ \phi_1(r)&=-2\pi Zer,\quad d=1\ .\end{aligned} \tag{2.2}$$

These then define the problem; to our knowledge only for $d=3$ is an exact bound-state energy-level formula known, namely the familiar result $-(Z^2/2n^2)e^2/a_0$, with n the principle quantum number and a_0 the Bohr radius $h^2/4\pi^2me^2$.

Therefore, in what follows, though we start from a formally exact Euler equation of density-functional theory for particles moving independently in the potentials (2.2), we shall evaluate the ratio $E/N\mu$ in the limit when the kinetic energy T as a functional of the electron density ρ can be approximated by its local-density value, plus corrections due to density gradients which are known to tend to zero relative to the local-density contribution when N and Z become sufficiently large. This is the asymptotic limit in which we calculate in the following section the ratio $E/N\mu$ as a function of dimensionality d.

III. EQUATION EXPRESSING CONSTANCY OF CHEMICAL POTENTIAL

In the original work of Thomas[6] and Fermi,[7] which led to modern density-functional theory,[2] the energy of the fastest electron, equal to the chemical potential μ, was written

$$\mu=\frac{p_F^2(r)}{2m}+V_d(r)\,. \tag{3.1}$$

In the present case, $V_d(r)=-e\phi_d(r)$ given in Eq. (2.2).

Density-functional theory replaces this equation (3.1) when combined with the phase-space relation[5]

$$\rho(r)=\frac{2\pi^{d/2}}{\Gamma(d/2+1)}\frac{p_F^d}{h^d} \tag{3.2}$$

by the formally exact equation

$$\mu=\frac{\delta T[\rho]}{\delta\rho(r)}+V_d(r)\,. \tag{3.3}$$

Unfortunately $T[\rho]$ is still only known for independent particles through density-matrix perturbation theory, not in closed form.[2]

Let us nevertheless multiply the Euler equation (3.3) by the electron density $\rho(r)$ and integrate over all space. Using the normalization condition

$$\int\rho\,d\tau=N \tag{3.4}$$

plus the constancy of μ in space, we then find

$$N\mu=\int\rho(r)\frac{\delta T[\rho]}{\delta\rho(r)}d\tau+\int\rho V_d(r)d\tau\,. \tag{3.5}$$

The writer[8] has estimated the difference between the kinetic term in Eq. (3.5) and the local electron gas kinetic energy for some simple potentials, and has shown in these examples that corrections to the local-density value of the kinetic energy are of lower order in the number of electrons N for large N.

Thus we can confidently return to the direct use of Eqs. (3.1) and (3.2) in obtaining the asymptotic limit we seek for $E/N\mu$ as a function of dimensionality d. Multiplying Eq. (3.1) by $\rho(r)$ as before and integrating over all space we find readily

$$N\mu=(1+2/d)T+U \tag{3.6}$$

where the potential energy U is simply $\int\rho V_d d\tau$ while T is the total local kinetic energy. But now, for the potentials (2.2) satisfying Poisson's equation, we have the virial theorem in the form[9]

$$2T+(d-2)U=0 \tag{3.7}$$

reducing to the usual well-known result $2T+U=0$ for $d=3$.

Putting these results (3.6) and (3.7) together with the fact that the eigenvalue sum E is clearly $T+U$ we find almost immediately the ratio $E/N\mu$ we were seeking, in the asymptotic limit of large N and Z, as

$$\frac{E}{N\mu}=\frac{d(4-d)}{4+2d-d^2}\equiv\alpha^{-1}\,. \tag{3.8}$$

This is the main result of the present paper. While the value of Z does not enter the above relation for $E/N\mu$ which is simply a function of dimensionality, it is clear that this function α^{-1} is specific to the class of bare point-charge potentials under investigation. Thus, for the d-dimensional free-electron gas the relation is

$$E/N\mu=(1+2/d)^{-1}\,, \tag{3.9}$$

which in fact follows immediately from Eq. (3.6) by putting $U=0$.

If, instead of the two examples just treated, we dealt with harmonic potentials in d dimensions, then since $T=U=\frac{1}{2}E$, we would obtain for the asymptotic limit of $E/N\mu$ simply $(1+1/d)^{-1}$. It will be noted that in all three examples $E/N\mu$ tends to unity as d tends to infinity.

IV. DISCUSSION AND SUMMARY

Since Eq. (3.8) is the central result of the paper, we have thought it worthwhile to record in Appendix A, by direct calculation of both E and μ, results specific to the logarithmic potential in Eq. (2.2). There, these results are compared and contrasted with those for $d=1$ and 3. The result (3.8) is thus directly verified to hold for these values of d.

However, returning to the virial theorem in Eq. (3.7), the next integer $d=4$ evidently corresponds to $E=T+U=0$ and this is reflected in the vanishing numerator of Eq. (3.8) for this dimensionality. If, in the light of this behavior for $d=4$ we choose to view $E/N\mu$ in Eq. (3.8) as a continuous function of d, then $E/N\mu$ goes from its correct value of 3 at $d=3$ through a singularity at $d=1+\sqrt{5}$, being negative for $1+\sqrt{5}<d<4$. We briefly record in Appendix B the nature of the expansions about this singular point.

If we exclude the pathological region $1+\sqrt{5}\leq d\leq 4$, there seems to be no difficulty in applying Eq. (3.8) for $d\geq 5$. Therefore, with the above region excluded, we note that if Eq. (3.8) is combined with the "thermodynamic" expression[10]

$$\mu=\left[\frac{\partial E}{\partial N}\right]_Z \tag{4.1}$$

Eqs. (3.8) and (4.1) can be integrated to yield

$$E(Z,N,d)=F(Z,d)N^{\alpha} \tag{4.2}$$

where the exponent α is given explicitly in terms of dimensionality d by Eq. (3.8).

Equation (4.2) can be readily confirmed for $d=3$ using an argument which follows Ref. 10. If we have $\mathcal{N}$ closed shells, then since a closed shell of principle quantum number n contains $2n^2$ electrons we find

$$E=-(Z^2e^2/a_0)\mathcal{N}\,, \tag{4.3}$$

while evidently

$$N=\sum_{1}^{\mathcal{N}}2n^2=\mathcal{N}(\mathcal{N}+1)(2\mathcal{N}+1)/3\,. \tag{4.4}$$

As N and $\mathcal{N}$ become truly large, this equation (4.4) has the obvious asymptotic solution $\mathcal{N}=(\frac{3}{2})^{1/3}N^{1/3}$ and hence

$$E(Z,N,d=3)=-(\tfrac{3}{2})^{1/3}Z^2N^{1/3}\,, \tag{4.5}$$

showing that $F(Z,d=3)=-(\frac{3}{2})^{1/3}Z^2$ in Eq. (4.2) and confirming that $\alpha=\frac{1}{3}$ as given by Eq. (3.8). Incidentally, it is worth remarking that the neutral atom energy discussed by Milne[11] long ago is proportional to $Z^{7/3}$ as in Eq. (4.5) with $N=Z$. The numerical coefficient $(\frac{3}{2})^{1/3}=1.1$ is reduced to 0.78 due to the screening by the self-consistent field. Finally, from Eq. (4.5) we can use Eq. (4.1) to find μ and taking the ratio $E/N\mu$ we confirm Eq. (3.8) for the case $d=3$.

It should be noted at this point, in connection with the use of Eqs. (3.1) and (3.2) rather than Eq. (3.3), that if we use the Thomas-Fermi density, this is not integrable[5] for $d\geq 4$. However, this does not seem to be a serious difficulty for the argument given here, as density gradient corrections remove such singular behavior without affecting the leading term in the energy for large N.

To conclude, the work in this paper gives a clear-cut example which confirms the conjecture made by Pucci and March[3,4] as to the central role of dimensionality in determining the limiting ratio of $E/N\mu$ as the total number of electrons becomes large. This may well lead to progress in interpreting results in molecules having fundamentally different shapes, corresponding to different dimensionalities d. Nevertheless, one must caution that the ratio $E/N\mu$ will only be dominated by dimensionality in cases where potentials belong to the same class as d is varied.

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APPENDIX A: ASYMPTOTIC PROPERTIES OF LOGARITHMIC POTENTIAL

As noted in the main text, only for the case $d=3$ do we have the exact bound-state level spectrum. As we saw in Eqs. (4.5) and (4.1) these levels led to explicit results for E and μ in the large-N limit.

The purpose of this appendix is to exhibit similar results for the logarithmic potential in Eq. (2.2) corresponding to $d=2$. Such a potential was used previously, for instance, by Dyson[12] in his study of a two-dimensional charged gas, and in a totally different context it has been employed as a model for quark confinement.[13,14] There the explicit potential energy used was

$$V(r)=\epsilon\ln(r/b)\ , \tag{A1}$$

and we shall therefore effect this minor generalization of Eq. (2.2) below. We recover the form (2.2) for $d=2$ by putting $\epsilon=2Ze^2$ and equating $\ln b$ to zero.

The electron density $\rho(r)$ is given by

$$\rho(r)=\frac{4\pi m}{h^2}[\mu-\epsilon\ln(r/b)] \tag{A2}$$

and μ is determined as usual by the normalization condition

$$N=\int\rho(r)2\pi r\,dr=\frac{4\pi m}{h^2}\int_0^{r_0}[\mu-\epsilon\ln(r/b)]2\pi r\,dr\ , \tag{A3}$$

where the semiclassical radius r_0 is given by

$$\mu=\epsilon\ln(r_0/b)\ \text{ or }\ r_0=b\exp(\mu/\epsilon)\ . \tag{A4}$$

After a short calculation, and putting $\epsilon=2Ze^2$, we obtain the chemical potential μ as

$$\frac{\mu}{Ze^2}=\ln\left[\frac{N}{Z}\right]+\ln\left[\frac{h^2b^{-2}}{4\pi^2me^2}\right]. \tag{A5}$$

Integrating Eq. (4.1), and dropping terms independent of N yields

$$\frac{E}{Ze^2}=N\ln(N/Z)-N+N\ln(h^2b^{-2}/4\pi^2me^2)\ . \tag{A6}$$

Forming $E/N\mu$ from Eqs. (A5) and (A6) leads in the large-N limit to the value unity given by Eq. (3.8) for $d=2$. Equations (A6) and (A5) are the two-dimensional analogs of Eq. (4.5) and the chemical potential derived from it using Eq. (4.1).

To conclude this appendix we briefly consider the linear potential corresponding to $d=1$ in Eq. (2.2). Such a potential was used by Lenard[15] for a one-dimensional charged gas and by Antippa and Phares[16] in the context of quark confinement. A brief calculation paralleling that given above for $d=2$ yields the chemical potential as

$$\mu=KZ^{2/3}N^{2/3}\ , \tag{A7}$$

where the known constant K depends only on the fundamental constants. Integrating Eq. (4.1) yields the corresponding asymptotic form of E for large N as

$$E=(\tfrac{3}{5})N\mu\ , \tag{A8}$$

agreeing again with Eq. (3.8) for $d=1$. It is worth observing that, for $N=Z$, both $d=1$ and $d=3$ have an eigenvalue sum proportional to $Z^{7/3}$ in leading order. For the two-dimensional case, the first logarithmic term drops out of Eq. (A6) on the point $N=Z$ and the energy is then $O(Z^2)$ in the limit of large Z.

APPENDIX B: EXPANSION OF $E/N\mu$ ABOUT SINGULAR POINT

Though we have, of course, the closed analytical formula (3.8) for $E/N\mu$ as a function of dimensionality d, approximate methods in vogue in statistical mechanics prompt us to add this further appendix. The first point which we simply note in passing is that $E/N\mu$ in Eq. (3.8) is merely the ratio of second-order polynomials in d in the asymptotic limit considered in this paper.

Secondly, we have noted the existence of a singular point at dimensionality $1+\sqrt{5}$, which we denote by d_s below. It would be natural, therefore, if one were seeking an approximate theory of $E/N\mu$, to expand this quantity around the singular point. Let us do this explicitly for the case $d<d_s$ by writing

$$d=d_s-\Delta,\ \ \Delta\text{ positive}\ . \tag{B1}$$

Then a short calculation demonstrates that, with the largely irrelevant proviso that $\Delta<2(d_s-1)$,

$$E/N\mu=\frac{a_1}{\Delta}+a_2+a_3\Delta+\cdots\ . \tag{B2}$$

Explicit expressions for the a's are, of course, readily obtained by inserting Eq. (B1) into Eq. (3.8); we merely give a_1 and a_2 as

$$a_1 = \frac{d_s(4-d_s)}{2(d_s-1)} \tag{B3}$$

and

$$a_2 = \frac{8-8d_s+3d_s^2}{20} . \tag{B4}$$

Inserting the numerical value of d_s we find $a_1 = 0.55$, $a_2 = 0.68$, and at $d = 3$ these terms contribute to the value 3 an amount $2.3 + 0.7$.

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