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Spatially dependent generalization of Kato's theorem for atomic closed shells in a bare Coulomb field

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For a bare Coulomb potential energy $-Ze^2/r$, it is shown that the total electron density $\rho(r)$ for an arbitrary number of closed shells is given by $\rho(r)=(2Z/a_0)\int_r^\infty \rho_s(r)dr$ where ρ_s is the s-state contribution to $\rho(r)$. This yields Kato's theorem $[\partial\rho(r)/\partial r]_{r=0}=(-2Z/a_0)\rho(r=0)$ as a limiting case. That $\partial\rho/\partial r$ is always negative follows, for all distances r. For the nth closed shell, with density $\rho_n(r)$, it is further shown that $R_{n0}(r)=[(-a_0/2Z)\partial\rho_n/\partial r]^{1/2}$, with R_{n0} the s-state radial wave function. This result can be used to construct an explicit differential equation for $\rho_n(r)$.

I. INTRODUCTION

In a recent study,[1] the bound-state Slater sum for electrons moving in a bare Coulomb potential energy $V(r)=-Ze^2/r$ has been related to that for s states, for arbitrary temperature. In the present paper, we consider the purely quantum-mechanical case of an arbitrary number of closed electronic shells in the bare Coulomb field defined above. The focal point is the total electron density $\rho(r)$, built by summing the density $\rho_n(r)$ of the nth closed shell over n.

The outline of the paper is as follows. In Sec. II we utilize a result of Blinder[2] that constitutes a generalization of Unsold's theorem. This allows the density $\rho_n(r)$ to be written in terms of the s-state radial wave function $R_{no}(r)$.[3] This result is used here to relate the total density $\rho(r)$ directly to that part, $\rho_s(r)$, contributed by the s states alone. This relation is shown to contain Kato's theorem[4,5]

$$(\partial\rho/\partial r)_{r=0}=(-2Z/a_0)\rho(r=0),\quad a_0=\hbar^2/me^2\ , \tag{1.1}$$

as a special case, and a spatially dependent generalization of Kato's theorem is thereby established for the Coulomb field. A further result that follows from this generalization is that $\partial\rho/\partial r<0$, proving that $\rho(r)$ is a monotonically decreasing function of r for any arbitrary number of closed shells in the Coulomb-field case.

Section III is then concerned with an individual closed shell. An explicit relation is written for the radial wave function $R_{no}(r)$ for s states in terms of $\rho_n(r)$ and it is pointed out that this can be used to derive a differential equation satisfied by $\rho_n(r)$. In the Appendix, the generalization of Kato's theorem established in the present paper for a Coulomb field is discussed in relation to approximate density-functional theories.

II. GENERALIZATION OF KATO'S THEOREM FOR COULOMB FIELD

Blinder's work [2]leads to the result[3]

$$\rho_n(r)=P_n'^2-P_nP_n''\ , \tag{2.1}$$

where $P_n=rR_{no}$ with R_{no} the s-state radial wave function for the principal quantum number n. P_n satisfies the Schrödinger equation

$$P_n''+\frac{2m}{\hbar^2}\left[\epsilon_n+\frac{Ze^2}{r}\right]P_n=0\ , \tag{2.2}$$

with ϵ_n denoting the usual hydrogenlike levels. However, we shall proceed to eliminate these by dividing both sides of Eq. (2.2) by P_n and then differentiating with respect to r. We thereby obtain

$$P_nP_n'''-P_n'P_n''=\frac{2m}{\hbar^2}\frac{Ze^2}{r^2}P_n^2\ . \tag{2.3}$$

Now the left-hand side of Eq. (2.3) is readily shown from Eq. (2.1) to equal $-\partial\rho_n/\partial r$, which yields

$$\frac{\partial\rho_n}{\partial r}=-\frac{2Z}{a_0}\rho_{no}\ , \tag{2.4}$$

where $\rho_{no}(r)$ denotes the s-state density $R_{no}^2=P_n^2/r^2$.

One can sum Eq. (2.4) over an arbitrary number of closed shells to relate the total density $\rho(r)$ thereby obtained to the s-state contribution to this density, $\rho_s(r)$, by

$$\frac{\partial\rho(r)}{\partial r}=-\frac{2Z}{a_0}\rho_s(r)\ . \tag{2.5}$$

Since $\rho_n(r)$ tends to zero as r tends to infinity, Eq. (2.5) can be integrated to obtain

$$\rho(r)=\frac{2Z}{a_0}\int_r^\infty \rho_s(r)dr\ . \tag{2.6}$$

Equation (2.5), or its integral (2.6), constitutes the desired generalization of Kato's theorem (1.1). Evidently, at $r=0$, the p, d, etc., states give zero contribution to $\rho(r=0)$ which is therefore simply equal to $\rho_s(r=0)$, and obviously Eq. (2.5) then reduces to Eq. (1.1) as $r\to 0$.

A further interesting consequence of Eq. (2.5) is that, since $\rho_s(r)>0$, $\partial\rho(r)/\partial r<0$, showing that the total electron density $\rho(r)$ decreases monotonically from the origin. The writer knows of no exception to this result for real atomic densities, although, of course, the present rigorous proof is restricted to the unscreened Coulomb field.

III. RADIAL s-STATE WAVE FUNCTION FOR nTH CLOSED SHELL RELATED TO ELECTRON DENSITY $\rho_n(r)$

Returning to Eq. (2.4), we can write, since the radial wave functions are real quantities,

$$R_{no} = \left[-\frac{a_0}{2Z} \frac{\partial \rho_n(r)}{\partial r} \right]^{1/2} , \tag{3.1}$$

where we have utilized the fact that $\partial \rho_n(r)/\partial r \leq 0$, the equality sign obviously corresponding to the nodes of $R_{no}(r)$. This relation (3.1) is of interest in relation to density-functional theory. In particular, such a functional relation between R_{no} and the electron density $\rho_n(r)$ could be made the basis for the use of the variational principle to determine $\rho_n(r)$. However, the resulting Euler equation for $\rho_n(r)$ can only be equivalent to that obtained by substituting $P_n = rR_{no}$, with R_{no} as in Eq. (3.1), into the Schrödinger equation (2.2). Using

$$P_n^2 = -(a_0/2Z) r^2 \rho_n' , \tag{3.2}$$

it is a straightforward matter to obtain a third-order nonlinear differential equation satisfied by $\rho_n(r)$. Since one would, of course, work with the linear equation (2.2) for P_n, we merely record this third-order equation in the Appendix.

IV. SUMMARY AND CONCLUSION

The main results of the present work are embodied in Eqs. (2.5) and (2.6) which constitute the desired generalization of Kato's theorem (1.1). These Eqs., valid for all r, yield the bonus that they establish that $\partial \rho/\partial r < 0$, which in turn means that $\rho(r)$ for the bare Coulomb field decreases monotonically with increasing r. We have noted that, to date, no exception is known to this inequality applied to real atomic densities, though, of course, this latter result is not proved by the present argument.

In addition, Eq. (3.1) demonstrates explicitly that the s-state radial wave function can be written in terms of the closed-shell electron density $\rho_n(r)$. This means that $\rho_n(r)$, if desired, can be determined from an explicit third-order, but nonlinear, differential equation. We have not, so far, found how to generalize this equation (A1) to apply to the total density $\rho(r)$ for an arbitrary number of closed shells. However, because the results of the model problem solved in this present work have interest for density-functional theory, we have thought it worthwhile in the Appendix to relate Eqs. (2.5) and (2.6) to the simplest form of density-functional theory, namely the Thomas-Fermi method.

APPENDIX: DIFFERENTIAL EQUATION FOR CLOSED-SHELL DENSITY $\rho_n(r)$ AND GENERALIZED KATO'S THEOREM RELATED TO DENSITY-FUNCTIONAL THEORY

We first record the differential equation satisfied by the electron density $\rho_n(r)$ of the nth closed shell. This is found by direct substitution of Eq. (3.1) for $R_{no} = P_n/r$ into Eq. (2.2). Then one can express the result in terms of $\rho_n(r)$ and its derivatives, plus the s-shell density $\rho_{no}(r)$ given by $P_n^2/r^2 = \rho_{no}(r)$. The final step is then to use Eq. (2.4) to eliminate $\rho_{no}(r)$. The third-order nonlinear differential equation for the closed-shell density $\rho_n(r)$ is

$$r\rho_n''' + 2\rho_n'' - \frac{1}{2} r \frac{\left[\rho_n''\right]^2}{\rho_n'} + \left[4Z - \frac{2Z^2}{n^2}\frac{r}{a_0}\right]\frac{\rho_n'}{a_0} = 0 , \tag{A1}$$

which is readily verified, for instance, to be satisfied by the K-shell density

$$\rho_1(r) = (Z^3/\pi a_0^3)\exp(-2Zr/a_0) .$$

Naturally by using Eq. (2.4) one could write an equivalent second-order differential equation for the s-state density $\rho_{no}(r)$.

In the second part of this Appendix, we shall consider briefly the relation of the generalization of Kato's theorem embodied in Eq. (2.5) to the simplest density-functional theory, namely the Thomas-Fermi method. Again for the Coulomb field, the Thomas-Fermi approximation to the total density $\rho(r)$ is[6]

$$\rho^{\mathrm{TF}}(r) = \frac{4\pi}{3h^3}(2m)^{3/2}\left[\mu + \frac{Ze^2}{r}\right]^{3/2} , \tag{A2}$$

where μ is the chemical potential of the electron cloud. One can write the derivative appearing in Eq. (2.5) as

$$\frac{\partial \rho^{\mathrm{TF}}(r)}{\partial r} = \frac{2\pi}{h^3}(2m)^{3/2}\left[\mu + \frac{Ze^2}{r}\right]^{1/2}\left[-\frac{Ze^2}{r^2}\right] . \tag{A3}$$

Next, one can obtain the s-state density by solving the one-dimensional Schrödinger equation (2.2) by a one-dimensional phase-space argument to obtain

$$r^2\rho_s^{\mathrm{TF}}(r) = \frac{2(2m)^{1/2}}{h}\left[\mu + \frac{Ze^2}{r}\right]^{1/2} . \tag{A4}$$

Substituting for $(\mu + Ze^2/r)^{1/2}$ from Eq. (A4) into Eq. (A3), one does indeed find a relation of the form of the generalization (2.5) of Kato's theorem, apart from the presence of a factor of order unity, from this simple approximate density-functional theory.

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[1] N. H. March, Phys. Lett. **111A**, 47 (1985).

[2] S. M. Blinder, Phys. Rev. A **29**, 1674 (1984).

[3] R. Shakeshaft and L. Spruch, J. Phys. B **18**, 1919 (1985).

[4] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[5] See also, for example, S. Fraga and G. Malli, *Many-Electron Systems: Properties and Interactions* (Saunders, Philadelphia, 1968).

[6] See, for example, N. H. March, *Self-Consistent Fields in Atoms* (Pergamon, Oxford, 1975).