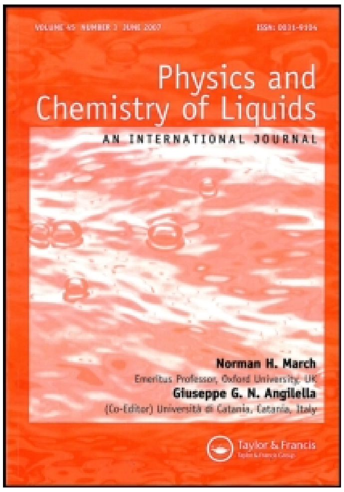

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SLATER SUM IN CYLINDRICALLY SYMMETRIC INHOMOGENEOUS ELECTRON LIQUIDS: TOWARDS A DIFFERENTIAL EQUATION FOR THE STARK EFFECT IN HYDROGEN ATOM

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Attention is focussed here on a variety of cylindrically symmetric inhomogeneous electron liquids. These include separable potentials in which a general variation along the (z) axis of cylindrical symmetry is combined with isotropic harmonic confinement in the (x,y) plane. In this case, an explicit differential equation is derived for the Slater sum along the z axis by projecting out of the (off-diagonal) canonical density matrix the states with zero angular momentum about the axis of symmetry. Some attention is then given to the calculation of the Slater sum for a hydrogen-like atom in a uniform electric field of arbitrary strength. The model of a separable potential with harmonic confinement, though no longer exact, is shown to lead directly to a (now approximate) equation for the Slater sum along the z axis for the Stark effect in hydrogen. Finally some further progress is shown to be possible in the extreme high field limit.

Keywords: Electron liquid; Slater sum; Stark effect

1. INTRODUCTION

We have been concerned in earlier work [1] with differential equations for the Slater sum $P(\vec{r}, \beta)$ in simple quantum-mechanical problems of physical interest, examples being (i) the bare Coulomb field, (ii) free

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electrons on to which are switched a uniform electric field of arbitrary strength F and (iii) an initially isotropic harmonic oscillator perturbed by such a field F. In each of the cases (i)–(iii), an exact differential equation now exists for $P(\vec{r}, \beta)$.

In the present work, we shall deal further with cylindrically symmetric systems. In fact, all three problems (i) to (iii) already are embraced by this classification. The long-term aim underlying the present study is to construct a differential equation for the Slater sum in the Stark problem for the hydrogen atom.

The outline of the present paper is therefore as follows. In Section 2 immediately below, we shall focus on the importance in cylindrically symmetric problems of projecting out the $m = 0$ states from the full Slater sum, *i.e.*, those states which have zero angular momentum around the z axis of cylindrical symmetry. Then in Section 3 a specific example is given of the Slater sum for initially free electrons in a uniform electric field of arbitrary strength. This example serves to illustrate the intimate relation between $P_{m=0}(z, \beta)$ and the full Slater sum, again, however, restricted to the z axis. This relation has therefore prompted us in Section 4 to consider in detail how to construct the Slater sum in the presence of a general cylindrically symmetric potential. Section 5 constitutes a summary, together with some suggestions for future work. The Stark effect in hydrogen, especially in the high field limit, is treated in the Appendices.

2. PROJECTION OUT OF SLATER SUM OF ZERO ANGULAR MOMENTUM ($m = 0$) STATES ABOUT THE CYLINDRICAL AXIS

In this section we focus all attention on projecting out the $m = 0$ states from the Slater sum $P(\vec{r}, \beta)$ which is the diagonal element ($\vec{r} = \vec{r}_1 = \vec{r}_2$) of the canonical density matrix $C(\vec{r}_1, \vec{r}_2, \beta)$ defined by

$$C(\vec{r}_1, \vec{r}_2, \beta) = \sum_{\text{all } i} \psi_i(\vec{r}_1)\, \psi_i^*(\vec{r}_2) \exp(-\beta\varepsilon_i) \quad : \beta = (k_B T)^{-1} \qquad (1)$$

where the ψ_i's are the normalized eigenfunctions, with corresponding eigenvalues ε_i, of the Hamiltonian

$$\hat{H}_{\vec{r}} = -\frac{\hbar^2}{2m}\nabla^2_{\vec{r}} + V(\vec{r}). \tag{2}$$

The canonical density matrix C satisfies the Bloch equation

$$\hat{H}_{\vec{r}_1}\, C(\vec{r}_1, \vec{r}_2, \beta) = -\frac{\partial C(\vec{r}_1,\ \vec{r}_2,\ \beta)}{\partial \beta} \tag{3}$$

with the completeness 'boundary' condition $C(\vec{r}_1,\ \vec{r}_2,\ 0) = \delta(\vec{r}_1 - \vec{r}_2)$. When the potential $V(\vec{r})$ is symmetrical under rotations around the z axis, $C(\vec{r}_1,\ \vec{r}_2,\ \beta)$ takes the form

$$C(\vec{r}_1, \vec{r}_2, \beta) = \sum_{m=-\infty}^{\infty} A_m \exp[im(\phi_1 - \phi_2)] \tag{4}$$

where ϕ_1 and ϕ_2 are the azimuthal angles of the points $\vec{r}_1$ and $\vec{r}_2$. Making use of the integral

$$W_m = \frac{1}{2\pi}\int_0^{2\pi} e^{im\phi} d\phi \tag{5}$$

which is one for $m = 0$ and zero in all other cases, one can formally project out the sum over the $m = 0$ states by integrating in the same way over $\phi_1 - \phi_2$, namely

$$C_{m=0}(\rho_1,\ z_1,\ \rho_2,\ z_2, \beta) = \frac{1}{2\pi}\int_0^{2\pi} C(\vec{r}_1,\ \vec{r}_2,\ \beta)\ d(\phi_1 - \phi_2) \tag{6}$$

where ρ is the cylindrical coordinate $\sqrt{x^2 + y^2}$.

It is important to analyze this projection by looking at the symmetry of the states considered in the summation. The states with $m = 0$, in fact, have a σ symmetry and are the unique states which do not have a node on the z axis. Hence, going on the diagonal and calculating the partial sum over the z axis ($x = y = 0$), one can recover the Slater sum as a function of z, namely

$$P(z,\ \beta) = P_{m=0}(z,\ \beta) = C_{m=0}(0,\ z,\ 0,\ z,\ \beta). \tag{7}$$

2.1. Example of Harmonic Oscillator in an Electric Field

To illustrate this result let us consider the case of an isotropic harmonic oscillator with frequency ω in a uniform electric field F directed along the z axis. The canonical density matrix has the known expression [2]

$$\begin{aligned} C(\vec{r}_1, \vec{r}_2, \beta) = & \left[\frac{\omega}{2\pi \sinh(\beta\omega)}\right]^{3/2} \exp\left(\frac{\beta F^2}{2\omega^2}\right) \\ & \times \exp\left[-\frac{\omega}{4}\tanh\left(\frac{\beta\omega}{2}\right)\left((x_1 + x_2)^2\right.\right. \\ & \left.\left. + (y_1 + y_2)^2 + \left(z_1 + z_2 - \frac{2F}{\omega^2}\right)^2\right)\right] \\ & \times \exp\left[-\frac{\omega}{4}\coth\left(\frac{\beta\omega}{2}\right)(\vec{r}_1 - \vec{r}_2)^2\right] \end{aligned} \tag{8}$$

which inserted in Eq. (6) gives the result

$$\begin{aligned} C_{m=0}(\rho_1, z_2, \rho_2, z_2, \beta) = & \left[\frac{\omega}{2\pi \sinh(\beta\omega)}\right]^{3/2} \exp\left(\frac{\beta F^2}{2\omega^2}\right) \\ & \times \exp\left[-\frac{\omega}{4}\tanh\left(\frac{\beta\omega}{2}\right)\right. \\ & \left.\left(\rho_1^2 + \rho_2^2 + \left(z_1 + z_2 - \frac{2F}{\omega^2}\right)^2\right)\right] \\ & \times \exp\left[-\frac{\omega}{4}\coth\left(\frac{\beta\omega}{2}\right)(\rho_1^2 + \rho_2^2 + (z_1 - z_2)^2)\right] \\ & \times I_0\left[-\frac{\omega}{2}\left(\tanh\left(\frac{\beta\omega}{2}\right) - \coth\left(\frac{\beta\omega}{2}\right)\right)\rho_1\rho_2\right] \end{aligned} \tag{9}$$

where I_0 is a Bessel function of imaginary argument of order zero. Equation (9) evaluated on the diagonal and over the z axis finally leads back to the full Slater sum, which is

$$\begin{aligned} P(z, \beta) = & \left[\frac{\omega}{2\pi \sinh(\beta\omega)}\right]^{3/2} \exp\left(\frac{\beta F^2}{2\omega^2}\right) \\ & \times \exp\left[-\omega \tanh\left(\frac{\beta\omega}{2}\right)\left(z - \frac{F}{\omega^2}\right)^2\right]. \end{aligned} \tag{10}$$

This intimate relation between the Slater sum calculated on the z axis and the sum over the $m = 0$ states suggests the derivation of a differential equation by expanding the partial density matrix $C_{m=0}$ about the diagonal to which we turn immediately below.

2.2. Expansion of *m* = 0 Projection of Canonical Density Matrix Near Diagonal

We follow the method given in our earlier work [1] but now working in cylindrical coordinates. Neglecting ϕ derivatives in the Hamiltonian we start from the two Bloch equations

$$\left[-\frac{1}{2\rho_1}\frac{\partial}{\partial\rho_1}\left(\rho_1\frac{\partial}{\partial\rho_1}\right)-\frac{1}{2}\frac{\partial^2}{\partial z_1^2}+V(\rho_1,\ z_1)\right]C_{m=0}=-\frac{\partial}{\partial\beta}C_{m=0} \quad (11)$$

$$\left[-\frac{1}{2\rho_2}\frac{\partial}{\partial\rho_2}\left(\rho_2\frac{\partial}{\partial\rho_2}\right)-\frac{1}{2}\frac{\partial^2}{\partial z_2^2}+V(\rho_2,\ z_2)\right]C_{m=0}=-\frac{\partial}{\partial\beta}C_{m=0} \quad (12)$$

in which the Laplacian has been written in terms of cylindrical coordinates.

Now using the new variables

$$\begin{cases} t_+ = \rho_1^2 + \rho_2^2 \\ t_- = \rho_1^2 - \rho_2^2 \\ z_+ = z_1 + z_2 \\ z_- = z_1 - z_2 \end{cases} \quad (13)$$

in the limits

$$t_+ \to 0 \quad t_- \to 0 \quad z_- \to 0 \quad (14)$$

and then summing and subtracting Eqs. (11) and (12) we have

$$\left[-4\frac{\partial}{\partial t_-}-2\frac{\partial^2}{\partial z_+\partial z_-}+V'(z_+/2)z_-\right]C_{m=0}=0 \quad (15)$$

$$\left[-4\frac{\partial}{\partial t_+}-\frac{\partial^2}{\partial z_+^2}-\frac{\partial^2}{\partial z_-^2}+2V(z_+/2)\right]C_{m=0}=-2\frac{\partial}{\partial\beta}C_{m=0}. \quad (16)$$

This system of differential equations will lead to an equation for the Slater sum provided the behaviour of $C_{m=0}$ near the diagonal and in proximity of the z axis is known.

Owing to the symmetry contraint the most general expression for $C_{m=0}$ up to the third order in length infinitesimals ($\Delta\rho$ or Δz) is

$$C_{m=0} = P(z_+/2,\beta) + a(z_+/2,\beta)t_+ + b(z_+/2,\beta)z_-^2 + c(z_+/2,\beta)t_- z_- + \delta_4 \tag{17}$$

where δ_4 indicates more generally infinitesimals of higher order. Equation (17) other than the Slater sum contains explicitly three more unknown functions to be determined. The three functions a, b and c are not completely independent.

3. DIRECT DETERMINATION OF SLATER SUM FOR INITIALLY FREE ELECTRONS IN A UNIFORM ELECTRIC FIELD

Having set out above a near-diagonal expansion of the canonical density matrix, it will be helpful to digress, before determining the functions a, b and c above, to give a direct calculation of the Slater sum of plane waves modified by an electric field, and to relate this to the $m = 0$ projection.

Starting from the Schrödinger equation in cylindrical coordinates for an electron in a uniform electric field F along the z axis

$$\left[-\frac{1}{2\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) - \frac{1}{2\rho^2}\frac{\partial^2}{\partial\phi^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} - Fz\right]\psi = E\psi \tag{18}$$

recognizing that for $m = 0$ the wavefunction does not depend on the variable ϕ, by setting

$$\begin{cases} E = E_1 + E_2 \\ \psi(\rho, z) = u(\rho)\, v(z) \end{cases} \tag{19}$$

and carrying out the separation we have

$$-\frac{1}{2\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial u}{\partial\rho}\right) = E_1 u \tag{20}$$

and

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial z^2} - Fz\right)v = E_2 v. \tag{21}$$

The partial sum $P_{m=0}(\rho, z, \beta)$ can be written formally as

$$P_{m=0}(\rho, z, \beta) = \sum_E \sum_{E_1+E_2=E} u^2(\rho)\, v^2(z) \exp[-\beta(E_1 + E_2)] \tag{22}$$

which can be factorized as follows

$$P_{m=0}(\rho, z, \beta) = \left(\sum_{E_1} u^2(\rho) e^{-\beta E_1}\right)\left(\sum_{E_2} v^2(z) e^{-\beta E_2}\right), \tag{23}$$

the functions u and v being depending respectively on E_1 and E_2.

The second factor in Eq. (23) is the well known Slater sum for an electron moving in a one dimensional space under a constant electric field [3]

$$P_F(z, \beta) = \frac{1}{(2\pi\beta)^{1/2}} \exp\left(\beta F z + \frac{\beta^3 F^2}{24}\right) \tag{24}$$

while the first factor can be calculated recognizing that the equation

$$v'' + \frac{1}{\rho} v' + 2E_1 v = 0 \tag{25}$$

is a Bessel equation solved by $J_0(\sqrt{2E_1}\rho)$. Inserting this solution in the 'sum' over E_1, making the substitution $E_1 = q^2/2$ and replacing the summation by an integration over $q^2/2$, one obtains [4]

$$\sum_{E_1} u^2(\rho) e^{-\beta E_1} = \lambda \int_0^\infty e^{-\beta q^2/2} J_0^2(q\rho)\, d\left(\frac{q^2}{2}\right) = \frac{\lambda}{\beta} \exp\left(-\frac{\rho^2}{\beta}\right) I_0\left(\frac{\rho^2}{\beta}\right) \tag{26}$$

where λ is a constant which must be taken as $1/2\pi$. Combining Eqs. (26) and (24) we have finally

$$P_{m=0}(\rho, z, \beta) = \frac{1}{(2\pi\beta)^{3/2}} \exp\left(\beta F z + \frac{\beta^3 F^2}{24}\right) \exp\left(-\frac{\rho^2}{\beta}\right) I_0\left(-\frac{\rho^2}{\beta}\right) \tag{27}$$

which corresponds to the diagonal elements of $C_{m=0}$ from Eq. (9) in the limit $\omega \to 0$.

4. SYSTEM OF DIFFERENTIAL EQUATIONS DETERMINING SLATER SUM ALONG AXIS OF SYMMETRY

This is the point at which to return to the determination of the functions a, b and c introduced in Section 2. Since considerable simplification results, we shall begin with the assumption that the potential energy $V(\rho, z)$ entering the Bloch Eq. (3) is separable in cylindrical coordinates.

4.1. Separability of Potential in Cylindrical Coordinates

When the cylindrically symmetric potential $V(\rho, z)$ takes the form $V_1(\rho) + V_2(z)$, by exploiting the same separation of variables given in the previous section, two new equations are derived for u and v defining the states with $m = 0$, namely,

$$\left[-\frac{1}{2\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + V_1\right]u = E_1 u \tag{28}$$

and

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial z^2} + V_2(z)\right)v = E_2 v. \tag{29}$$

In the limits (14), to which our attention is focussed, we can integrate equation (28) near $\rho = 0$ by expanding u in a power series of ρ truncated at the second order.

Making the assumption that $V_1(0)$ is finite, up to the second order u is given by

$$u(\rho) = u(0)\left[1 + \frac{1}{2}(V_1(0) - E_1)\rho^2 + \cdots\right]. \tag{30}$$

Now we can sum over all the possible $m = 0$ eigenstates in order to get the following two-dimensional partial canonical density matrix for small values of ρ_1 and ρ_2

$$C_1(\rho_1, \rho_2, \beta) = P_1(0,\ \beta) + \frac{1}{2}\left(V_1(0)\, P_1(0,\ \beta) + \frac{\partial P_1(0,\ \beta)}{\partial \beta} \right)(\rho_1^2 + \rho_2^2) \tag{31}$$

where the sum P_1 at the point $\rho = 0$ has the same value of the corresponding two-dimensional full Slater sum because the states with $m \neq 0$ have a node at the origin.

Switching attention to the z dependence we must expand near the diagonal the one-dimensional canonical density matrix

$$C_2(z_1,\ z_2,\ \beta) = \sum_{E_2} v(z_1)\, v^*(z_2) e^{-\beta E_2}. \tag{32}$$

Using variables z_+ and z_- defined in Eq. (13) we have

$$\begin{aligned} v(z_1) &= v(z_+/2) + \frac{1}{2}\, v'(z_+/2) z_- + \frac{1}{8} v''(z_+/2) z_-^2 + \cdots \\ v(z_2) &= v(z_+/2) - \frac{1}{2}\, v'(z_+/2) z_- + \frac{1}{8} v''(z_+/2) z_-^2 + \cdots \end{aligned} \tag{33}$$

and using Eq. (29) to replace second derivatives after few simple manipulations we can write

$$\begin{aligned} C_2(z_1,\ z_2,\ \beta) = P_2(z_+/2, \beta) + \Bigg[& V_2(z_+/2)\, P_2(z_+/2,\ \beta) \\ & - \frac{1}{8} P_2''(z_+/2,\ \beta) + \frac{\partial P_2(z_+/2,\ \beta)}{\partial \beta} \Bigg] z_-^2 + \cdots \end{aligned} \tag{34}$$

Multiplying C_1 by C_2 one gets $C_{m=0}$ expanded near the diagonal and near the z axis in the form (17) with an explicit expression for the functions a, b and c, namely

$$\begin{aligned} a(z) &= \frac{1}{2}\left[V_1(0)\, P(z) + P_2(z) \frac{\partial P_1(0)}{\partial \beta} \right] \\ b(z) &= V_2(z)\, P(z) + P_1(0) \frac{\partial P_2(z)}{\partial \beta} - \frac{1}{8} P''(z) \\ c(z) &= 0 \end{aligned} \tag{35}$$

where the implicit dependence on β has been omitted and where $P(z) = P_1(0)\,P_2(z)$ is the full three-dimensional Slater sum evaluated over the z axis. It is important to remark that c results as identically zero when the full potential is separable in cylindrical coordinates while a and b satisfy the relation

$$2a + b = VP + \frac{\partial P}{\partial \beta} - \frac{P''}{8} \tag{36}$$

which is instead quite general, as we will show below, for cylindrically symmetric potentials.

4.2. General Cylindrically Symmetric Potential

In order to study the more general problem we turn to the differential Equations (15) and (16) which are solved by the expansion (17) for $C_{m=0}$.

Inserting the expression (17) in (15) and (16) the following two new equations are readily obtained

$$\begin{cases} 2c + b' = 1/2\, V'P \\ 2a + b = VP + \partial P/\partial\beta - 1/8\, P'' \end{cases} \tag{37}$$

in which P and V are assumed evaluated at $\rho = 0$.

The system of Eq. (37) shows clearly a relation of the three unknown functions a, b and c with the Slater sum and the potential. In the cases we have considered in our earlier work [1], namely (i) the Coulomb potential, (ii) the uniform electric field and (iii) the harmonic potential, the functions a and c can be explicitly expressed in terms of b and the Slater sum. Projecting out the $m = 0$ states from the canonical density matrix and by expanding following Eq. (17), the Table I can be easily generated using respectively the Blinder's variables [5] for the Coulomb potential, the Janussis' solution [3] for the uniform electric field and the Sondheimer and Wilson solution [6] for the harmonic potential.

The functions reported in Table I for the cases (i)–(iii) when inserted in the system (37) lead to the same differential equations for the Slater sum obtained in our earlier work [1]. In this context it is important to remark that for a central field, owing to isotropicity, it is

TABLE I Functions a and c from Eq. (17) in terms of b and the Slater sum evaluated over the z axis for different model potentials

Potential	$a(z, \beta)$	$c(z, \beta)$
$-(Z/r)$	$b + (P'/4z)$	$-(P'/8z^2)$
$-Fz$	b	0
$(1/2)\omega^2 r^2$	$b + (P'/8z)$	0
$(1/2)\omega^2 r^2 - Fz$	$b + (P'/8(z - F/\omega^2))$	0
$-(Z/r) - Fz$	$b - 2zc$	c [A]

[A] This result involves the ansatz (38).

sufficient to know the behaviour of the Slater sum over the positive z axis to complete the knowledge of the Slater sum itself.

Turning to the table the last row refers to the Stark effect. In this case the expression given for $a(z, \beta)$ is not proved but was obtained making the ansatz

$$c = \frac{1}{2z}(b - a) \tag{38}$$

which is valid for the separate cases (i), the Coulomb potential, and (ii), the uniform electric field. Making this assumption from the system (37) one can readily derive the following differential equation relating P and c:

$$\frac{1}{8}P''' - \left(V + \frac{\partial}{\partial\beta}\right)P' + \frac{1}{2}V'P = 4zc' + 10c. \tag{39}$$

Works actually in progress are considering the proof of the ansatz (38) and the way to determine explicitly c in order to transform the Eq. (39) into a differential equation for the Slater sum evaluated over the z axis in the Stark effect.

4.3. Harmonic Confinement of Electrons in a General Potential Varying Along the z Axis

It is of some interest now to discuss a last example in which perpendicularly to the axis of cylindrical symmetry is switched on a field of harmonic forces and along the z axis a more general field. The potential has the separable form $(1/2)\omega^2\rho^2 + V(z)$. In the Appendix 1 this simple potential will be related to a model which simulates the Stark effect given an appropriate choice of ω and of $V(z)$. Here we limit ourselves to show the derivation of an exact differential equation for the Slater sum along z. Again from the system (37) putting $c = 0$ and eliminating b we have

$$\frac{1}{8}P''' - \left(V + \frac{\partial}{\partial\beta}\right)P' - \frac{1}{2}V'P = -2a. \tag{40}$$

From Eq. (35) and substituting

$$P_1(0,\ \beta) = \frac{\omega}{2\pi\sinh(\beta\omega)} \tag{41}$$

we have finally

$$\frac{1}{8}P''' - \left[\omega\coth(\beta\omega) + V + \frac{\partial}{\partial\beta}\right]P' - \frac{1}{2}V'P = 0 \tag{42}$$

which is valid for any given potential V varying along z.

5. SUMMARY AND FUTURE DIRECTIONS

In calculating the Slater sum generated by cylindrically symmetric potentials, it is shown in the present paper that there is considerable merit in projecting out the $m = 0$ states, corresponding to zero angular momentum about the z axis of cylindrical symmetry. Thus, in Section 2, it is demonstrated that the Slater sum near to the z axis is characterized by three functions, a, b and c, of only one spatial variable. Furthermore, a quite general equation is established relating a and b to the cylindrically symmetric potential. It is further shown that if the original cylindrically symmetric potential $V(\rho, z)$, with $\rho = \sqrt{x^2 + y^2}$, is itself separable, then the third function c above is identically zero. This enables a complete solution to be given for a potential in the form $(1/2)\omega^2\rho^2 + V(z)$.

This has led us into the final part of the article: towards a differential equation for the (on z axis) Slater sum $P(z, \beta)$ for the Stark effect in the hydrogen-like atom. Here away from the axis the potential energy

$$V(\rho,\ z) = -Fz - \frac{Z}{\sqrt{\rho^2 + z^2}} \tag{43}$$

with Z the atomic number in the hydrogen-like system, is evidently cylindrically symmetric but not, however, separable in cylindrical coordinates (rather in parabolic coordinates). By analogy with the zero field case $F = 0$ in Eq. (43), the function $c \neq 0$. However, an ansatz has been proposed, generalizing the known result for $F = 0$ to non-zero F, for the function c, and this has allowed us to make an entry in Table I for $F \neq 0$, though, of course, the ansatz on which the entry is based remains to be established.

Finally, it is relevant to refer to the high field work of Benassi *et al.* [7]. These authors study mainly the 'ground-state': which in their language has a finite lifetime, as first discussed by Oppenheimer [8]. They argue that, for $Z = 1$, the ground-state energy E in the limit of large F has a leading term in its high-field expansion of the form

$$E \propto (F \ln F)^{2/3}. \tag{44}$$

The factor $e^{-\beta E_i}$ appearing inside the summation over levels in the Slater sum suggests therefore that an 'independent' variable of the form $\{\beta(F \ln F)^{2/3}\}$ should enter $P(\vec{r}, \beta)$ in the high field limit. This is to be contrasted with the variable $\beta^3 F^2 \equiv \{\beta F^{2/3})\}^3$ entering the free-field form of the Slater sum discussed earlier in Section 3. It is, presumably, the 'interaction' between the two terms in the potential (43) in the high field limit that modifies the free-field variable $\beta F^{2/3}$ above to the form (for $Z = 1$) $\beta F^{2/3}(\ln F)^{2/3}$ (compare Appendices 2 and 3).

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APPENDIX 1. MODELLING THE STARK EFFECT BY HARMONIC CONFINEMENT

The potential (43), referring to the Stark effect, can be expanded, near the z axis and for large z, up to second order in ρ, namely

$$V(\rho,\ z) = -Fz - \frac{Z}{|z|}\left(1 - \frac{\rho^2}{2z^2}\right) + \cdots \tag{A.1}$$

In this regime perpendicularly to the axis the electron is subjected to elastic forces of 'constant'

$$\omega^2 = \frac{Z}{|z|^3}. \tag{A.2}$$

This consideration has led us to formulate an approximate differential equation for the Slater sum substituting ω from Eq. (A.2), as a function of z now, into Eq. (42) in order to build a model for the Stark effect along the axis of symmetry. The equation

$$\frac{1}{8}P''' - \left[\omega(z)\coth(\beta\omega(z)) + V(z) + \frac{\partial}{\partial\beta}\right]P' - \frac{1}{2}V'(z)P = 0, \tag{A.3}$$

where

$$V(z) = -Fz - \frac{Z}{|z|}, \tag{A.4}$$

may eventually be amenable to solution by numerical techniques.

APPENDIX 2. SCALING OF ENERGIES IN STARK PROBLEM FOR HYDROGENIC ATOM WITH EXTREMELY HIGH FIELD *F* AND NUCLEAR CHARGE *Z*

Benassi *et al.* [7] demonstrate that in the extreme high field limit (see their Eq. 14)

$$f(\omega) = \zeta \tag{A.5}$$

where

$$\omega = F^{1/3}/(-2E)^{1/2}; \quad \zeta = 4Z/F^{1/3}. \tag{A.6}$$

Therefore

$$-2E = \frac{F^{2/3}}{\omega^2} \tag{A.7}$$

and since from Eq. (A.5)

$$\omega = g(\zeta) \tag{A.8}$$

one finds

$$-2E = \frac{F^{2/3}}{h(4Z/F^{1/3})}. \tag{A.9}$$

Consider now the relation (44) with $Z = 1$

$$E \propto F^{2/3}(\ln F)^{2/3}. \tag{A.10}$$

This must mean that for large F (and $Z = 1$) the function h in Eq. (A.9) has the form

$$\frac{1}{h} \propto (\ln F)^{2/3}. \tag{A.11}$$

But the variable in h, as seen in Eq. (A.9), for $Z \neq 1$ is proportional to $Z/F^{1/3}$, hence

$$\frac{1}{h} \propto (\ln (F/Z^3))^{2/3}. \tag{A.12}$$

Thus, inserting this variable F/Z^3 into the logarithm in Eq. (44), one reaches the desired form

$$E \propto F^{2/3}\left\{ \ln\left(\frac{F}{Z^3}\right)\right\}^{2/3}. \tag{A.13}$$

Naturally, in taking the form of h in Eq. (A.9) as in Eq. (A.12), one has passed to the high field limit.

Hence returning to the factor $e^{-\beta E_i}$ in the Slater sum for (now high field limit) the Stark effect one has the exponent

$$\beta F^{2/3}\left\{ \ln\left(\frac{F}{Z^3}\right)\right\}^{2/3}, \tag{A.14}$$

showing, as anticipated in the text, that the $\{\ln(F/Z^3)\}^{2/3}$ behaviour modifying the free field variable $\beta F^{2/3}$ in the high field limit cames from interaction between the field and the Coulomb nucleus carrying charge Z. If, in the high field limit, Z was (somewhat artificially) taken as constant $F^{1/3}$, the one sees from Eq. (A.14) that one variable $\beta F^{2/3}$ of the free field Slater sum is regained in this high field 'Stark-like' regime.

APPENDIX 3. USE OF EFFECTIVE POTENTIAL MATRIX TO RELATE BARE COULOMB FIELD AND HYDROGEN STARK EFFECT

The purpose of this Appendix is to point out that the effective potential matrix $U(\vec{r}_1, \vec{r}_2, \beta)$ may afford a way to relate the bare Coulomb field problem (see Tab. I of this article) and the hydrogen Stark effect. Following Hilton *et al.* [9] (see also [10]) we write the canonical density matrix C_{ZF} for the hydrogen Stark effect as

$$C_{ZF}(\vec{r}_1, \vec{r}_2, \beta) = C_{Z0}(\vec{r}_1, \vec{r}_2, \beta)\exp[-\beta U_{ZF}(\vec{r}_1, \vec{r}_2, \beta)]. \tag{A.15}$$

Here $F = 0$ is the bare Coulomb problem. If in Eq. (A.15) we now put Z (the nuclear charge in atomic units) equal to zero, then from Section 3 it follows immediately that

$$U_{0F}(\vec{r}_1, \vec{r}_2, \beta) = -\frac{1}{2}F(z_1 + z_2) - \frac{\beta^2 F^2}{24}. \tag{A.16}$$

Thus, U is a natural enough tool to 'switch' the electric field F on to the bare Coulomb field density matrix C_{Z0}. Substituting Eq. (A.15) into the Bloch Eq. (3), and using the same equation for $F = 0$, one is led to the following equation for U_{ZF}, the Coulomb potential $-Z/r$ only now appearing implicitly through the presence of C_{Z0}

$$\left[1+\beta\frac{\partial}{\partial\beta}-\beta\frac{\vec{\nabla}_1 C_{Z0}}{C_{Z0}}\cdot\vec{\nabla}_1-\frac{\beta}{2}\nabla_1^2\right]U_{ZF}(\vec{r}_1,\vec{r}_2,\beta)=V(\vec{r}_1)-\frac{1}{2}\beta^2|\vec{\nabla}_1 U_{ZF}|^2. \tag{A.17}$$

Putting $Z = 0$

$$C_{00} = \frac{1}{(2\pi\beta)^{3/2}}\exp\left(-\frac{|\vec{r}_1-\vec{r}_2|^2}{2\beta}\right) \tag{A.18}$$

and it is readily verified by putting C_{00} in Eq. (A.17) that Eq. (A.16) is the desired physical solution.

In the high field regime we can return to the free field result (A.16) and note that, provided we keep $(z_1 + z_2)$ bounded, the F^2 term will eventually dominate. This has motivated us to make the assumption that in the case $F \to \infty$, already considered in Appendix 2,

$$U_{ZF}(\vec{r}_1,\ \vec{r}_2,\ \beta) \equiv U_{ZF}(\rho_1,\ z_1,\ \rho_2,\ z_2,\ \beta).$$

This then allows the $m = 0$ projection to be made from Eq. (A.15) to yield

$$C_{ZF}^{m=0} = C_{Z0}^{m=0}\exp[-\beta U_{ZF}(\rho_1,\ z_1,\ \rho_2,\ z_2,\ \beta)]. \tag{A.19}$$

This equation, combined with Eq. (A.17), can be used by insertion of the earlier expansion (see Tab. I) of $C_{ZF}^{m=0}$ and the bare Coulomb field $C_{Z0}^{m=0}$, but we shall not pursue the detail here.