Interaction of atoms, molecules, and ions with constant electric and magnetic fields

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A thorough unified treatment is given of the quantum-mechanical operators and wave functions for a molecular system (composed of N moving charged particles) in static uniform electric and magnetic fields $\underline{E}$ and $\underline{B}$. The treatment is rigorous within the nonrelativistic approximation. The system may either be neutral or charged. The fields may have arbitrary intensities and orientations. Close correspondence is maintained between the classical and quantum-mechanical treatments. The wave functions are expressed both in the time-independent energy representation and in time-dependent wave packets. Three types of momentum play important roles. For single-particle systems they are the *canonical* momentum $\underline{P}$, the *mechanical* momentum $\underline{\Pi}=\underline{P}-(e/c)\underline{A}=M\underline{\dot{R}}$, and the *pseudomomentum* $\underline{\mathcal{K}}=\underline{\Pi}-(e/c)\underline{R}\times\underline{B}-e\underline{E}t$. The pseudomomentum is a constant of the motion. Except in the absence of magnetic fields, not all of the components of either $\underline{\Pi}$ or $\underline{\mathcal{K}}$ commute. This complicates the quantum-mechanical formalism. The components of the pseudomomentum have simple classical interpretations, and in quantum mechanics they are related to the operator which performs a boost to a reference frame moving with constant velocity $\underline{v}$. In this moving frame, the electric field intensity is $\underline{E}'=\underline{E}+(\underline{v}/c)\times\underline{B}$. Thus, in a frame moving with the drift velocity $\underline{v}_d=(c/B^2)\underline{E}\times\underline{B}$, the components of the electric field intensity perpendicular to $\underline{B}$ vanish. In this paper, the velocity boost operators are used to show the relationships between wave functions expressed in reference frames moving with repsect to each other. The dynamics of the N-particle systems are simplified by making the Power-Zienau-Woolley transformation (which reduces as a special case to a unitary transformation used by Lamb) and by using center-of-mass and internal coordinates. Generalizing previous works, it is shown how the pseudomomentum is involved in separating these degrees of freedom for N particles in both $\underline{E}$ and $\underline{B}$. For neutral molecules, the Schrödinger equation is "pseudoseparated" and the internal degrees of freedom are coupled to the center of mass motion only by the "motional Stark Effect," which involves the constant of motion $\underline{\mathcal{K}}$. For ionic systems, only one component of the center of mass is coupled to the internal motion. Quantitative estimates of the weak center-of-mass coupling are made for both neutral and ionic $n=1$ and $n=2$ quantum states of two-body systems by perturbation expansions in powers of the field strengths. In the usual nonrigorous treatments of systems in magnetic fields, no distinction is made between $\underline{\Pi}$ and $\underline{\mathcal{K}}$ and both are approximated by $M\underline{\dot{R}}$, where M is the mass of the molecule and $\underline{R}$ is taken to be the classical orbital position of a single particle having the same mass and charge. This is an excellent approximation for ground-state molecules and ions in weak fields. However, the resulting errors can be much larger if the system is in either intense fields or high-lying states (e.g., Rydberg levels). These are the conditions under which the rigorous formalism should be most useful. The determination of the wave functions and energy levels for many-particle ionic systems is complicated due to the coupling with the center of mass. The suggestion is made that it might be useful to boost the reference frame so that it moves with the velocity $\underline{\dot{R}}$ of a single classical particle. The Schrödinger equation in this frame could serve as a more suitable basis for perturbative or variational treatments.

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I. INTRODUCTION

This paper is intended to be a unified treatment of nonrelativistic N-particle kinematics in constant fields. It encompasses both charged and neutral molecules, and applies to uniform electric and magnetic fields, $\underline{E}$ and $\underline{B}$, of arbitrary strengths and orientations. As a warm-up, the classical and quantum-mechanical solutions for a single particle are reviewed, with close attention paid to their correspondences. A focal point of the investigation is the concept of boosting to a moving reference frame, a transformation which gives rise to a motional electric field. This is very familiar classically, but the associated changes in the quantum-mechanical operators and wave functions have tended to remain somewhat obscure. Both stationary states and wave packets are discussed here, requiring the use of the time representation for full generality, but in some situations it is possible to restrict attention to the energy representation.

For molecular systems, description of the center-of-mass (CM) motion by wave packets is also considered, although the emphasis is on the dynamical operators and on separation of CM degrees from the stationary-state wave functions. The exact form of the field-induced coupling between CM and internal coordinates is shown to depend on the choice of reference frame (and gauge, of course), a fact which can sometimes be used to tactical advantage. The formal derivations for N-particle systems are carried out as far as can be done without considering particular systems. Specific applications are then made for the low-lying states of two-body systems in magnetic fields.

A general goal of a previous series of papers (Yang and Hirschfelder, 1980; Yang, Hirschfelder, and Johnson, 1981; Hirschfelder, Yang, and Johnson, 1982) is a solid theoretical foundation for treatment of CM motion in problems where the effects of external fields must be taken into account. [An example might be the modification of atomic velocities by resonant radiation—see, for example, Gordon and Ashkin, 1980; Ashkin, 1980; Cook, 1980.] These papers considered molecular systems in arbitrary time- and space-varying semiclassical fields, retaining all degrees of freedom and semirelativistic corrections of relative order α^2, where α is the fine-structure constant. In the present article, advantage is taken of the much greater simplicity inherent in constant fields in the nonrelativistic approximation. We hope that this will form a basis for a parallel semirelativistic treatment, using the formalism of the earlier work.

For a *single particle* of charge e and mass M in constant electric and magnetic fields, $\underline{E}$ and $\underline{B}$, there are three momentumlike vectors which are important, quantum mechanically and classically.

(1) The *canonical momentum* $\underline{P}$, all of whose components commute or have vanishing Poisson brackets;

(2) The *mechanical momentum,* $\underline{\Pi}=\underline{P}-(e/c)\underline{A}$, which represents mass times velocity; and

(3) The *pseudomomentum,* $\underline{\mathscr{K}}=\underline{\Pi}+(e/c)\underline{B}\times\underline{R}-e\underline{E}t$, which is a constant of the motion.

Here $\underline{A}$ is the vector potential and c the speed of light. The properties mentioned are each unique to the particular momentumlike quantity, and are not generally shared by the other two. For instance, not all of the components of $\underline{\Pi}$, nor those of $\underline{\mathscr{K}}$, commute with each other (unless $e=0$ or $\underline{B}=0$). The pseudomomentum was derived for $\underline{E}=0$ by Johnson and Lippmann (1949), and then for combined fields by Bacry, Combe, and Richard (1970a, 1970b). Its components, in addition to having simple classical interpretations, may quantum mechanically be diagonalized in different ways so as to produce different types of wave functions.

For an N-particle system in which the particles interact through potentials invariant with respect to space and velocity translations, each of these momenta has an analog which is the sum of those for the individual particles. Thus the *total canonical momentum* is the momentum conjugate to the CM, the *total mechanical momentum* represents the total mass times the CM velocity, and the total *pseudomomentum* is a constant of the motion which is important in separating CM and internal degrees of freedom. The latter is familiar from (or sometimes implicit in) a body of literature dealing with separation of the CM in a constant magnetic field (Lamb, 1952; Elliott and Loudon, 1959, 1960; Gor'kov and Dzyaloshinskii, 1967; Breitenberger, 1968; Carter, 1967,1969a; Grotch and Hegstrom, 1971; Ryvkin, 1975; Avron, Herbst, and Simon, 1978,1981; O'Connell, 1979; Wunner and Herold, 1979; Pavlov-Verevkin and Zhilinskii, 1980; Wunner, Ruder, and Herold, 1980,1981a,1981b; Herold, Ruder, and Wunner, 1981). These papers provide the basis for much of our work, since clean separation of CM and internal coordinates is blocked only by magnetic-field-induced coupling terms in the kinetic energy operators. Whether or not an electric field is present, it is possible to eliminate (at least some of the) CM degrees of freedom by diagonalizing components of the total pseudomomentum. Whether one can separate all of the degrees of freedom depends on whether the system is neutral.

When the system is *electrically neutral,* all three components commute. The wave function may then be taken to be an eigenfunction of the total pseudomomentum with vector eigenvalue $\hbar\underline{K}$, leading to *pseudoseparation* of the CM. This means that the Schrödinger equation is reduced to an effective one involving only the internal coordinates, but dependent upon the eigenvalue $\hbar\underline{K}$. To be precise, the effective electric field in the internal equation is $\underline{E}+(\hbar/Mc)\underline{K}\times\underline{B}$, where M is the total mass. This was first demonstrated for $\underline{E}=0$ by Lamb in his paper on the hydrogen atom in a magnetic field (Lamb, 1952); that an external electric field could easily be included for neutral systems was pointed out by Carter (1967) and by Gor'kov and Dzyaloshinskii (1967).

The occurrence of the effective electric field is pertinent to applications involving the *motional Stark effect* (Blumberg, Itano, and Larson, 1979; Crosswhite, Lu, Fano, and Rau, 1979; Panock, Rosenbluh, Lax, and Miller, 1980a,

1980b). The fields in a frame moving with respect to the laboratory frame at constant velocity $\underline{v}$ are given by, through lowest orders in $\underline{v}/c$ (Landau and Lifshitz, 1975; Jackson, 1975),

$$\underline{E}'=\underline{E}+\frac{1}{c}\underline{v}\times\underline{B}\ , \tag{1.1}$$

$$\underline{B}'=\underline{B}\ . \tag{1.2}$$

A common interpretation is then that $\underline{E}+(\hbar/Mc)\underline{K}\times\underline{B}$ is the electric field in the rest frame of the CM, which is assumed to move at the constant velocity $\hbar\underline{K}/M$. Such an interpretation is not strictly correct, as has been emphasized by Avron, Herbst, and Simon (1978,1981) and Herold, Ruder, and Wunner (1981), since $\hbar\underline{K}$ is not the eigenvalue of the total *mechanical* momentum (which is also not a constant of the motion). In fact, the latter authors demonstrate that $\hbar\underline{K}/M$ is not even the average CM velocity, although we show that this should be a good approximation for low-lying states in magnetic fields which are weak on an atomic scale. This provides some justification for the usual (but hasty) assumption that the velocitylike quantity in the effective electric field seen by the internal degrees of freedom is simply the velocity of the molecule.

For an *ionic* system, the two components of the total pseudomomentum perpendicular to the $\underline{B}$ axis do not commute, so that, in addition to the Hamiltonian, a maximum of two commuting constants of the motion may be diagonalized from these components. The full Schrödinger equation is then reduced to an effective one in which a single CM degree of freedom remains coupled to the internal coordinates. Which degree of freedom this is depends upon whether or not $\underline{E}$ has a component $\underline{E}_\perp$ perpendicular to $\underline{B}$. If it does, the coupled coordinate is the Cartesian coordinate in the direction of $\underline{E}_\perp$. If it does not, there is some choice in the matter.

According to Eqs. (1.1) and (1.2), the question of whether $\underline{E}_\perp=0$ clearly depends upon the frame of reference. Boosting from the laboratory frame to the *drift frame,* which moves with the constant drift velocity

$$\underline{v}_d=\frac{c}{B^2}\underline{E}\times\underline{B}\ , \tag{1.3}$$

causes $\underline{E}'_\perp$ to vanish. The magnetic field $\underline{B}$ and the parallel component of $\underline{E}$, called $\underline{E}_{||}$, are unaffected by the nonrelativistic boost. (We shall frequently say simply that $\underline{E}_\perp=0$ in the drift frame and $\underline{E}_\perp\neq0$ in the lab frame.) Thus, as viewed from the drift frame, cylindrical symmetry exists and the external fields are parallel. For a classical particle, the orbit transverse to $\underline{B}$ is then described as the circular orbit expected in a magnetic field. When viewed from the lab frame, the symmetry is broken and the orbit is no longer circular.

Quantum mechanically, one requires a unitary transformation to boost to a moving frame. The operator accomplishing this is known for a free particle and is generalized here to account for the presence of the external fields. (It is closely related to the pseudomomentum.) We are thus able to show quite explicitly how motional electric fields enter into the Hamiltonian under a velocity boost. Knowing the explicit unitary transformation which accomplishes this, one then knows the exact relationship between the wave functions in the two frames. In particular, the single-particle wave functions for $\underline{E}_\perp\neq0$ can be derived from those for $\underline{E}_\perp=0$. This transformation generally depends upon the time, but is shown to be equivalent to a time-independent transformation in some circumstances. For instance, although there are different classes of stationary-state wave functions appropriate to the drift frame, only one remains a stationary state when boosted to the lab frame. This provides a slightly different slant on the symmetry breaking mentioned in the last paragraph.

The boost operation can be carried over to the molecular case, so that the N-particle wave functions and energies in the lab frame can be related to those in the drift frame. Thus it is only necessary to perform calculations in the drift frame; this is very advantageous for ionic systems where, as mentioned before, one has a choice of which CM degree of freedom is coupled to the internal coordinates. One choice corresponds to a variation on the usual ideas of CM elimination, a variation which was discussed by Avron, Herbst, and Simon (1978), and which is shown here to be related to quantizing the component along $\underline{B}$ of the total canonical orbital angular momentum about the origin. A detailed examination is made of the drift-frame stationary states, and it is demonstrated how the effects of CM motion can be evaluated by solving coupled equations in the internal coordinates. (The coupling disappears in the limit of vanishing magnetic field.)

All of these calculations are simplified by first performing another unitary transformation. Starting from the representation in which the individual particles are minimally coupled to the external fields, the *Power-Zienau-Woolley* (PZW) transformation is used to convert to the multipolar gauge (Power and Zienau, 1959; Woolley, 1971; Babiker, Power, and Thirunamachandran, 1974; Power, 1978). This modifies the Hamiltonian so that the CM is explicitly coupled to the internal coordinates only through the electric dipole moment operator. It also brings the total pseudomomentum to single-particle form (explained in the text). Although defined for general electromagnetic fields and gauges and numbers of particles, this unitary transformation reduces as a special case to that used by Lamb and others for a two-body system in a magnetic field. Actually, the N-particle version has appeared previously within the context of choice of gauge for molecular magnetic field Hamiltonians (Weisenthal and de Graaf, 1971; Moss and Perry, 1972; Sutter, Guarnieri, and Dreizler, 1970). We have not seen the connection with the PZW transformation pointed out before.

Applications of the theoretical developments are made to the ground and first excited states of the two-body Coulomb system in magnetic fields weak on an atomic scale. (Nonrelativistically, the electric field poses no complications with respect to CM separation.) For the *neutral case,* it is shown by perturbation theory that the average velocity of the CM (in the plane perpendicular to $\underline{B}$) is *proportional* to $\hbar\underline{K}/M$, which is the quantity entering the

motional electric field seen by the internal degrees of freedom. This constant of proportionality differs from unity by only one part in 10^{11}–10^{12} for $n=1$ and $B=10^5$ G. The deviation from unity for some states in the $n=2$ level is 5 orders of magnitude larger for the same field strength (as a consequence of the extra degeneracy of the excited levels), but is still very small.

For a *two-body ion* such as $^4He^+$, the coupling terms in the Hamiltonian are treated exactly within perturbation theory, allowing a comparison with the conventional one-body results based on the infinite nuclear mass limit. For the ground state, the one-body treatment gives an energy expansion in even powers of the magnetic field which agrees well with the even powers obtained by treating the helium ion as a two-body problem. For instance, the fractional difference in the diamagnetic susceptibilities is only about one part in 10^7. However, the two-body treatment introduces odd powers into the expansion, and a series of almost-equally-spaced levels emerges with energy splittings on the order of the nuclear hyperfine structure. It is shown that the small coupling terms between the CM and relative coordinates do not contribute to the energy until order B^3 for $n=1$, but can enter at order B^2 for $n=2$ (again a consequence of the extra degeneracy).

The importance of the extra degeneracy is that, in the appropriate gauge, the CM is coupled to the internal coordinates through the instantaneous electric dipole moment. For a field-free system with degenerate states of opposite parity, one can take linear combinations of these states such that the average dipole moment does not vanish (the well-known linear Stark effect). Thus the effects of the coupling are expected to be enhanced in cases like hydrogen or polyatomic symmetric top molecules with permanent dipole moments.

The rigorous treatment given in this paper is expected to be particularly useful, for example, for

(1) the spectral changes associated with the motional Stark effect and its influence on the transition probabilities in the neighborhood of avoided energy crossings, where the small energies associated with the motional Stark effect become important;

(2) molecules and ions in very intense electric and magnetic fields;

(3) energy levels of high Rydberg states of molecules and ions in fields;

(4) energy levels of van der Waals molecules in fields;

(5) electric and magnetic susceptibilities of molecules with permanent multipole moments;

(6) excitons, muonium, positronium, or other systems, for which one does not have extremely large mass ratios.

The organization is as follows. Section II is devoted to the single charged particle in combined fields and the way in which velocity boosts are implemented quantum mechanically. The operators for an N-body system of arbitrary overall charge are treated in Sec. III. Section IV deals with the neutral molecule wave functions and the motional Stark effect in the hydrogen atom. The wave functions for ionic systems and the charged two-body example are examined in Sec. V.

II. SINGLE PARTICLE IN CONSTANT FIELDS

A. Hamiltonian and constants of motion

In order to treat the motion of an ion in constant fields, it is first necessary to understand the dynamics of the corresponding single charged particle. (An uncharged particle, of course, does not interact with the fields, and is simply free.) The total Hamiltonian is taken as

$$H_{\rm tot}=H+H_{\rm spin} \ . \tag{2.1}$$

The *spin Hamiltonian* is

$$H_{\rm spin}=\frac{ge}{2Mc}\underline{B}\cdot\underline{s} \ , \tag{2.2}$$

where the particle has charge e, mass M, spin $\underline{s}$, and gyromagnetic factor g. This contributes only a constant term to the energy when $\underline{s}$ is quantized along $\underline{B}$. The spin is completely decoupled from the orbital motion at the level of precision considered here.

We shall be concerned with only the *orbital Hamiltonian,*

$$\begin{aligned} H&=\frac{1}{2M}\Pi^2+e\phi(\underline{R},t) \\ &=\frac{1}{2M}\left[\underline{P}-\frac{e}{2c}\underline{B}\times\underline{R}\right]^2-e\underline{E}\cdot\underline{R} \ . \end{aligned} \tag{2.3}$$

Here $\underline{\Pi}$ is the mechanical momentum of the particle,

$$\begin{aligned} \underline{\Pi}&=M\dot{\underline{R}}=\underline{P}-\frac{e}{c}\underline{A} \\ &=\underline{P}-\frac{e}{2c}\underline{B}\times\underline{R} \ , \end{aligned} \tag{2.4}$$

with $\underline{P}$ the canonical momentum ($-i\hbar\nabla$ in quantum mechanics) and the dot denoting total time differentiation. The vector and scalar potentials are chosen to be in the *static symmetric* gauge,

$$\begin{aligned} \underline{A}&=\tfrac{1}{2}\underline{B}\times\underline{R} \ , \\ \phi&=-\underline{E}\cdot\underline{R} \ , \end{aligned} \tag{2.5}$$

where we have the constant and uniform fields

$$\begin{aligned} \underline{B}&=(0,0,B) \ , \\ \underline{E}&=\underline{E}_\perp+\underline{E}_{||}=(0,E_\perp,E_{||}) \ , \end{aligned} \tag{2.6}$$

so that $B_z=B$, $E_y=E_\perp$, and $E_z=E_{||}$.

The Newtonian equations of motion obtained from H are then

$$\dot{\underline{\Pi}}=M\ddot{\underline{R}}=e\underline{E}+\frac{e}{c}\dot{\underline{R}}\times\underline{B} \ . \tag{2.7}$$

The special circumstance that $\underline{E}$ and $\underline{B}$ are constant vectors allows Eq. (2.7) to be rearranged as

$$\frac{d}{dt}\mathscr{K}=0 \ , \tag{2.8}$$

with

$$\underline{\mathscr{K}} = M\dot{\underline{R}} + \frac{e}{c}\underline{B}\times\underline{R} - e\underline{E}t - M\underline{v}_d$$

$$= \underline{P} + \frac{e}{2c}\underline{B}\times\underline{R} - e\underline{E}t - M\underline{v}_d \ . \tag{2.9}$$

The vector constant of the motion $\underline{\mathscr{K}}$ is called the pseudomomentum [extending the nomenclature used by Avron, Herbst, and Simon (1978) for $E=0$]. Johnson and Lippmann (1949) described $\underline{\mathscr{K}}$ and its significance when only a magnetic field is present. Bacry, Combe, and Richard (1970a,1970b) later derived it for the general case. It is generally both time and gauge dependent in form. For gauges other than the choice in Eqs. (2.5), the Hamiltonian, mechanical momentum, and pseudomomentum are given by the first lines of Eqs. (2.3), (2.4), and (2.9), respectively. The constant term $M\underline{v}_d$, where [from Eq. (1.3)]

$$\underline{v}_d = \frac{c}{B^2}\underline{E}\times\underline{B} = \hat{\underline{x}}(cE_\perp/B) \ , \tag{2.10}$$

has been included in the definition of $\underline{\mathscr{K}}$ for later convenience. In using Eq. (2.10), we assume that B does not vanish unless $E_\perp = 0$. However, v_d can be greater than c if $E_\perp > B$.

In component form, $\underline{\Pi}$ and $\underline{\mathscr{K}}$ are

$$\Pi_x = P_x + \frac{M\omega Y}{2} \ ,$$

$$\Pi_y = P_y - \frac{M\omega X}{2} \ , \tag{2.11}$$

$$\Pi_z = P_z \ ,$$

and

$$\mathscr{K}_x = P_x - \frac{M\omega Y}{2} - Mv_d \ ,$$

$$\mathscr{K}_y = P_y + \frac{M\omega X}{2} - eE_\perp t \ , \tag{2.12}$$

$$\mathscr{K}_z = P_z - eE_{||}t \ ,$$

where the *cyclotron frequency,*

$$\omega = \frac{eB}{Mc} \ , \tag{2.13}$$

is *twice the Larmor frequency,* and is *positive* or *negative,* depending on the sign of the charge e.

There will be occasions later when it is convenient to use the *zero-electric-field* form of $\underline{\mathscr{K}}$, which is denoted by $\underline{\mathscr{K}}^0$:

$$\underline{\mathscr{K}}^0 = \underline{P} + \frac{e}{2c}\underline{B}\times\underline{R} \ . \tag{2.14}$$

Its components are obtained from Eq. (2.12) by setting $E_\perp = 0$ and $E_{||} = 0$.

All of the above equations are valid in both classical and quantum mechanics. A brief review of the classical trajectories and the significance of the components of the pseudomomentum is provided next. This is followed by the quantum-mechanical applications of these constants of the motion.

B. Classical solution

The first line of Eq. (2.9) may be solved for $\underline{R}$ in terms of the six integration constants K_x, K_y, K_z, ρ, θ, and Z_0:

$$X = \rho\sin(\omega t+\theta) + \frac{\hbar K_y}{M\omega} + \frac{cE_\perp}{B}t \ ,$$

$$Y = \rho\cos(\omega t+\theta) - \frac{\hbar K_x}{M\omega} \ , \tag{2.15}$$

$$Z = Z_0 + \frac{\hbar K_z t}{M} + \frac{eE_{||}t^2}{2M} \ .$$

We have replaced the components of $\underline{\mathscr{K}}$ by those of $\hbar\underline{K}$ to emphasize that they are simple constants and to anticipate their connection with quantum-mechanical eigenvalues in later sections. Here Z is uniformly accelerated with initial position Z_0 and initial velocity $\hbar K_z/M$.

The orbit in the X-Y plane is trochoidal (Landau and Lifshitz, 1975). Figure 1 shows one of the three types of trochoidal trajectories. It is more easily described in the drift frame,

$$\underline{R}' = \underline{R} - \underline{v}_d t \ , \tag{2.16}$$

whose origin moves with respect to that of the laboratory frame at the drift velocity. The X'-Y' orbit (Fig. 2) is the circular orbit of a particle in a magnetic field. This, as explained in Sec. I, agrees with the fact that $\underline{E}'_\perp = 0$ in this frame, so that the fields are just $\underline{E}_{||}$ and $\underline{B}$.

The center of the X'-Y' orbit is stationary and is related to the transverse coordinates of the pseudomomentum by

$$(X_c, Y_c) = \left(\frac{\hbar K_y}{M\omega}, -\frac{\hbar K_x}{M\omega}\right) \tag{2.17}$$

or

$$\hbar\underline{K}_\perp = \frac{e}{c}\underline{B}\times\underline{R}_c \ , \tag{2.18}$$

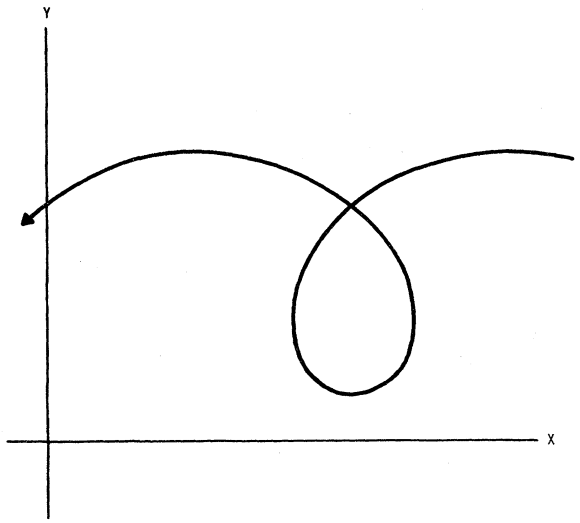

FIG. 1. Trochoidal orbit of a charged particle in perpendicular electric and magnetic fields.

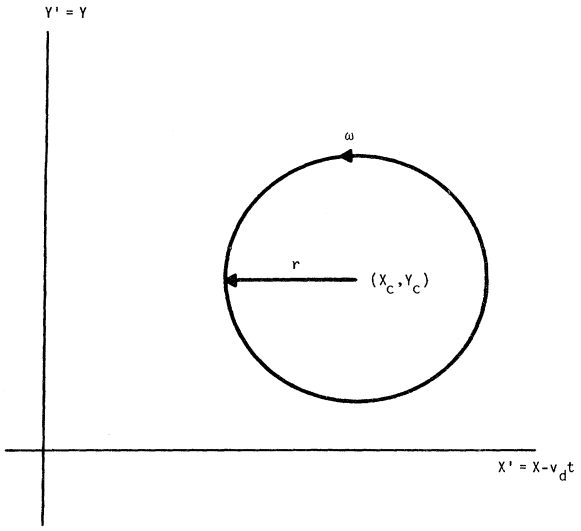

FIG. 2. Circular orbit of a charged particle in a magnetic field.

where $\underline{K}_\perp$ and $\underline{R}_c$ are two-dimensional vectors lying in the X'-Y' plane. The particle executes uniform circular motion about $\underline{R}_c$ with the cyclotron frequency ω and radius ρ. The energy of the two-dimensional orbit in the drift frame is, from Eqs. (2.15),

$$\mathscr{E}_{\perp d}=\frac{M}{2}(\dot{X}'^2+\dot{Y}'^2)=\frac{M}{2}\omega^2\rho^2 . \tag{2.19}$$

As a consequence of rotational symmetry about the center of the orbit, $\mathscr{E}_{\perp d}$ does not depend on θ. The lack of dependence of $\mathscr{E}_{\perp d}$ upon $\mathscr{X}_x$ and $\mathscr{X}_y$, and hence the coordinates of the center of the orbit, is a consequence of the translational invariance associated with a uniform magnetic field.

In contrast, the energy of the X-Y orbit as measured in the lab frame is

$$\begin{aligned}\mathscr{E}_{\perp l}&=\frac{M}{2}[\dot{X}^2+\dot{Y}^2]-eE_\perp Y\\&=\tfrac{1}{2}M\omega^2\rho^2+v_d\hbar K_x+\tfrac{1}{2}Mv_d^2 .\end{aligned} \tag{2.20}$$

By Eqs. (2.10), (2.13), and (2.17), $v_d\hbar K_x=-eE_\perp Y_c$, which is the time average of $-eE_\perp Y$. Thus the perpendicular electric field breaks the symmetry and makes the energy dependent upon the integration constant K_x. Geometrically, the center of the orbit now moves uniformly at the drift velocity $\underline{v}_d$.

The range of validity of the classical nonrelativistic solutions remains to be discussed. Imposing the boundary condition that the initial velocity vanishes, $\dot{\underline{R}}(t=0)=0$, upon Eqs. (2.15) leads to

$$\begin{aligned}\dot{X}&=v_d(1-\cos\omega t) ,\\ \dot{Y}&=v_d\sin\omega t ,\\ \dot{Z}&=eE_{||}t/M .\end{aligned} \tag{2.21}$$

To remain in the nonrelativistic domain, it is necessary that

$$\frac{1}{c}|\dot{Z}|=|eE_{||}t/Mc|\ll 1 \tag{2.22}$$

and

$$\frac{1}{c}[\dot{X}^2+\dot{Y}^2]^{1/2}=\frac{2E_\perp}{B}|\sin(\omega t/2)|\ll 1 . \tag{2.23}$$

The inequality in (2.22) is eventually violated as t grows unless $E_{||}=0$. The inequality in (2.23) is satisfied for all time if $E_\perp\ll B$ (in Gaussian units). If $E_\perp\gtrsim B$, on the other hand, this reduces to

$$|eE_\perp t/Mc|\ll 1 , \tag{2.24}$$

which is independent of B and identical in form to (2.22).[1]

Having shown that the classical solutions are of simpler nature in the drift frame, we now turn our attention to the quantum-mechanical solutions in the lab and drift frames. In order to do this, it is first necessary to understand in general how the velocity boost is performed in quantum mechanics.

C. Quantum-mechanical velocity boosts

It is generally assumed without proof that the lab-frame Hamiltonian H in Eq. (2.3) has the same form in a moving frame, with the exception that the fields $\underline{E}'$ and $\underline{B}'$ of Eqs. (1.1) and (1.2) are inserted in place of $\underline{E}$ and $\underline{B}$. If one can prove the unitary equivalence of the Hamiltonians in the two frames, one can then find the explicit relationship between the wave functions, and it seems profitable to search for the unitary operator which corresponds to a velocity boost.

For a *free particle,* this transformation is well known (Foldy, 1956, 1961; Shirokov, 1957), both nonrelativistically and relativistically. The equations of motion governed by Hamiltonian,

$$H_0=\frac{P^2}{2M} , \tag{2.25}$$

are invariant under the operations of the Galilean group. This includes, for instance, the familiar group of rotations in three dimensions, generated by the angular momentum operator $\underline{L}=\underline{R}\times\underline{P}$. It also includes the operation of shifting to a moving reference frame, for which the generator is the constant of motion

$$\underline{G}_0=M\underline{R}-\underline{P}t . \tag{2.26}$$

[1]The implication is that a nonrelativistic treatment is fully justified only for $E_{||}=0$ and $E_\perp\ll B$. This is, of course, violated frequently in the laboratory, but is not usually of concern. The relevant question is the *time scale* on which the motion of a system remains nonrelativistic. There is still a slight philosophical problem in switching to the drift frame if $E_\perp>B$ ($v_d>c$), since the light cones of special relativity are not being respected. Nevertheless, the mathematics are still valid, and this transformation between frames whose relative velocity exceeds the speed of light must be interpreted according to Galilean theory.

(That is, $\underline{G}_0$ commutes with $H_0 - i\hbar\partial/\partial t$.)

The unitary transformation

$$U = \exp(-i\underline{v}\cdot\underline{G}_0/\hbar) \tag{2.27}$$

has the effect [making use of the Baker-Campbell-Hausdorf formula; see Wilcox (1967)] of changing $\underline{R}$, $\underline{P}$, and H into

$$\underline{R}_U = U\underline{R}U^\dagger = \underline{R}' + \underline{v}t \ , \tag{2.28}$$

$$\underline{P}_U = U\underline{P}U^\dagger = \underline{P}' + M\underline{v} \ , \tag{2.29}$$

and

$$H_U = UHU^\dagger - i\hbar U\left[\frac{\partial}{\partial t}U^\dagger\right] = \frac{P'^2}{2M} \ . \tag{2.30}$$

The primes have been added to the operators $\underline{R}$ and $\underline{P}$ as a temporary bookkeeping device to denote that we have made a *passive* transformation.[2] Although they are the same operators as $\underline{R}$ and $\underline{P}$, representing the position and momentum of the particle, they are now measured from a new (moving) origin, as described in Fig. 3. Hereafter the primes are dropped and the fact that $\underline{R}$ and $\underline{P}$ have distinct meanings in the two representations should be implicitly understood.

Just as in classical canonical transformations (Goldstein, 1950), the Hamiltonian has a term that arises from the time dependence of the transformation. This term, $-i\hbar U(\partial U^\dagger/\partial t)$, cancels all terms involving $\underline{v}$ that stem from $UHU^\dagger$. We say that the Hamiltonian is *form invariant* under the boost since it still describes a free particle in the moving frame.

The state function is, of course, affected, as well. If the original wave function is the plane-wave stationary state,[3]

$$\Psi = \exp(i\underline{k}\cdot\underline{R} - i\hbar k^2 t/2M) \ , \tag{2.31}$$

the wave function in the new representation is

$$\begin{aligned}\Psi_U = U\Psi &= \exp(-iM\underline{v}\cdot\underline{R}/\hbar - iMv^2 t/2\hbar) \\ &\quad\times\exp(i\underline{v}\cdot\underline{P}t/\hbar)\Psi \\ &= \exp[i(\hbar\underline{k} - M\underline{v})\cdot\underline{R}/\hbar - i(\hbar\underline{k} - M\underline{v})^2 t/2M\hbar] \ .\end{aligned} \tag{2.32}$$

Here we have used the identity (Wilcox, 1967)

$$e^{a+b} = e^a e^b e^{-1/2[a,b]} \ , \tag{2.33}$$

which is valid if a and b both commute with $[a,b] = ab - ba$.

It is to be observed that this is a trivial example, since the same results can be obtained working strictly in an energy representation: the time-independent parts of Ψ and Ψ_U are then connected just by the time-independent part of U, i.e., $\exp(-iM\underline{v}\cdot\underline{R}/\hbar)$. In considering wave packets, the full time-dependent unitary transformation is necessary.

We now consider a particle in combined $\underline{E}$ and $\underline{B}$, which requires a new unitary transformation

$$U = \exp(-i\underline{v}\cdot\underline{G}/\hbar) \ , \tag{2.34}$$

where $\underline{G}$ has to be defined so that, in analogy to Eqs. (2.28) and (2.29),

$$\underline{R}_U = U\underline{R}U^\dagger = \underline{R} + \underline{v}t \tag{2.35}$$

and

$$\underline{\Pi}_U = U\underline{\Pi}U^\dagger = \underline{\Pi} + M\underline{v} \ . \tag{2.36}$$

The primes on the right sides are now implicit. Note that it is the *mechanical momentum* $\underline{\Pi}$, not the canonical momentum $\underline{P}$, which is to be boosted. This is justified classically by the fact that only the independent Newtonian variables $\underline{R}$ and $\dot{\underline{R}}$ of the Lagrangian formulation have physical significance (Yang, 1976; Cohen-Tannoudji, Din, and Laloë, 1977, pp 315–328; Kobe and Smirl, 1978) and can be measured at any given instant. In switching to Hamiltonian mechanics, $\underline{P} = M\dot{\underline{R}} + e\underline{A}/c$ assumes independent variable status instead of $\dot{\underline{R}}$, but $\underline{P}$ must be considered derived, depending as it does upon the measurable velocity and the choice of vector potential. Quantum mechanically, Eq. (2.36) is a statement that U must merely change the operator form of $\underline{\Pi}$ by a constant.

In contrast to the free-particle example, in general we *do* expect the Hamiltonian here to change under the boost. It is anticipated that the new Hamiltonian will still

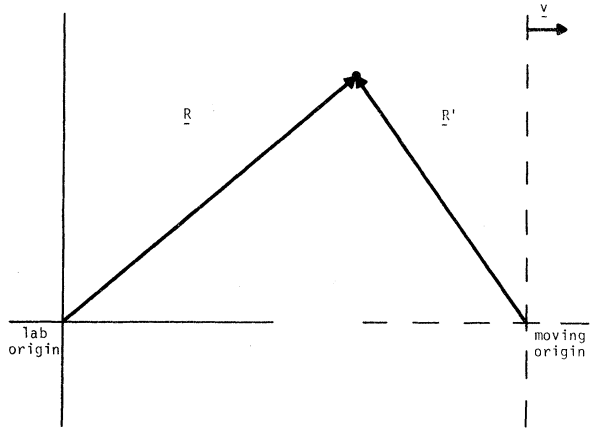

FIG. 3. Passive transformation to a moving reference frame. $\underline{R}$: Position of the particle as measured from the lab frame. $\underline{R}'$: Position of the particle as measured from the moving frame.

[2]A passive transformation changes the reference axes and leaves the particle motion unchanged, while an active transformation changes the particle motion and leaves the axes unchanged. See Messiah (1961).

[3]Since time dependence is of major concern in this paper, the definition of *stationary state* used here is that the wave function $\Psi(\underline{R},t)$ is of the separable form $\psi(\underline{R})\exp(-i\mathscr{E}t/\hbar)$, where $\mathscr{E}$ is constant and $\psi(\underline{R})$ is referred to as the *time-independent* wave function.

describe a particle in electric and magnetic fields, but now the fields must be the ones appropriate to the new frame, which are given in Eqs. (1.1) and (1.2). Thus, in addition to Eqs. (2.35) and (2.36), it is also required that

$$H_U = UHU^\dagger - i\hbar U\left[\frac{\partial}{\partial t}U^\dagger\right]$$

$$= \frac{\Pi^2}{2M} - e\left[\underline{E} + \frac{1}{c}\underline{v}\times\underline{B}\right]\cdot\underline{R} \ . \tag{2.37}$$

These three conditions determine the form of $\underline{G}$ up to a constant vector, as we shall now outline. If one attempts to use the free-particle boost generator $\underline{G}_0 = M\underline{R} - \underline{P}t$, it is seen that Eq. (2.35) is satisfied. However, this is also true if, in $\underline{G}_0$, one replaces $\underline{P}$ by either the mechanical momentum $\underline{\Pi}$ or the pseudomomentum $\underline{\mathscr{K}}$.

The second condition, Eq. (2.36), settles the question of which of the three momentumlike operators to use. From Eqs. (2.11) and (2.12), the nonvanishing commutators among all nine components are

$$[P_x,\Pi_y] = -[P_y,\Pi_x] = -[P_x,\mathscr{K}_y] = [P_y,\mathscr{K}_x] = \frac{ie\hbar B}{2c} \ , \tag{2.38}$$

$$[\Pi_x,\Pi_y] = -[\mathscr{K}_x,\mathscr{K}_y] = \frac{ie\hbar B}{c} \ . \tag{2.39}$$

From Eq. (2.38), it can be seen that, for example, $[G_{ox},\Pi_y]\neq 0$, since $[P_x,\Pi_y]\neq 0$. An attempt to boost in the x direction with G_{0x} therefore fails, because the operators Π_x and Π_y *both* undergo changes, in contradiction of Eq. (2.36). Substitution of P_x by Π_x is also unsatisfactory, since $[\Pi_x,\Pi_y]\neq 0$. However, all components of $\underline{\mathscr{K}}$ commute with all those of $\underline{\Pi}$, so that the generator $M\underline{R} - \underline{\mathscr{K}}t$ turns out to satisfy both Eqs. (2.35) and (2.36).

Actually, $\underline{G}$ is still arbitrary up to a time-dependent vector function $\underline{f}(t)$,

$$\underline{G} = M\underline{R} - \underline{\mathscr{K}}t - \underline{f}(t) \ . \tag{2.40}$$

Substitution of Eq. (2.40) into the last condition, Eq. (2.37), shows that we must have

$$\underline{f} = \underline{f}_0 + e\underline{E}t^2/2 + M\underline{v}_d t \ ,$$

with $\underline{f}_0$ an unimportant constant vector which is set equal to zero.

The final form for the Galilean velocity boost generator modified to account for the external fields is thus

$$\underline{G} = M\underline{R} - \left[\underline{P} + \frac{e}{2c}\underline{B}\times\underline{R} - e\underline{E}t/2\right]t$$

$$= M\underline{R} - \int_0^t d\tau\left[\underline{P} + \frac{e}{2c}\underline{B}\times\underline{R} - e\underline{E}\tau\right] \ . \tag{2.41}$$

[We obtained this before learning that it had been given in a related context by Bacry, Combe, and Richard (1970a, 1970b). These authors were more concerned with the operations which do not change the fields.] If $\underline{E}=0$ in the first place, $\underline{G}$ is seen to assume the simpler form

$$\underline{G}^0 = M\underline{R} - \underline{\mathscr{K}}^0 t \ . \tag{2.42}$$

For completeness, we give the form of the pseudomomentum under transformation by U of Eqs. (2.34) and (2.41):

$$\underline{\mathscr{K}}_U = \underline{P} + \frac{e}{2c}\underline{B}\times\underline{R} + M(\underline{v} - \underline{v}_d) - e\left[\underline{E} + \frac{1}{c}\underline{v}\times\underline{B}\right]t \ . \tag{2.43}$$

There is a complication that was not present in the free-particle example. Using Eqs. (2.39) and (2.41), we see that G_x and G_y do not commute:

$$[G_x,G_y] = -\frac{ie\hbar Bt^2}{c} \ . \tag{2.44}$$

Two successive boosts then lead to, using Eq. (2.33),

$$\exp(-i\underline{v}'\cdot\underline{G}/\hbar)\exp(-i\underline{v}\cdot\underline{G}/\hbar)$$

$$= \exp[-i(\underline{v}+\underline{v}')\cdot\underline{G}/\hbar + (iet^2/2\hbar c)\underline{B}\cdot\underline{v}'\times\underline{v}] \ . \tag{2.45}$$

Thus the composite transformation depends upon the order in which the boosts are performed through a time-dependent phase factor, unless $\underline{v}$ and $\underline{v}'$ are parallel or unless one of them is parallel to $\underline{B}$.

The motion in Z is separable from that in X and Y, and thus the boost operator is factorable. It has been treated in full for purposes of unity. Note that, for $\underline{v}$ in Eq. (2.34) parallel to $\underline{B}$, we have

$$U = \exp\left[-i\frac{v}{\hbar}(MZ - P_z t + eE_{||}t^2/2)\right] \ . \tag{2.46}$$

Since G_z is a constant of the motion, U leaves H unchanged, as is evident from Eq. (2.37).

The other special case of interest is $\underline{v}=\underline{v}_d$, the drift velocity in Eq. (2.10). The perpendicular electric field then vanishes from the Hamiltonian. This is discussed further in Sec. II.E, where the wave functions for $E_\perp\neq 0$ are derived from those for $E_\perp = 0$ (summarized next).

D. Wave functions with $E_\perp = 0$

The Z-dependent part of H in Eq. (2.3) always separates from the other coordinates. If $E_\perp$ is zero, then

$$H = H_\perp^0 + H_{||} \ , \tag{2.47}$$

where

$$H_\perp^0 = \frac{1}{2M}(\Pi_x^2 + \Pi_y^2) \ , \tag{2.48}$$

$$H_{||} = \frac{1}{2M}P_z^2 - eE_{||}Z \ . \tag{2.49}$$

The two-dimensional Hamiltonian $H_\perp^0$ occurs for a particle in a pure magnetic field, while $H_{||}$ corresponds to a particle in a pure electric field. For future reference some known wave functions for these Hamiltonians are summarized here. Wave packets are discussed in Sec. II.F.

1. Electric field

There are at least two familiar solutions to the time-dependent Schrödinger equation in an electric field,

$$\left[H_{||}-i\hbar\frac{\partial}{\partial t}\right]\Psi_{||}(Z,t)=0\ . \tag{2.50}$$

The first is the stationary state

$$\Psi_{||}(Z,t)=\psi_{||}(Z)e^{-i\mathscr{E}t/\hbar}\ ,$$

where (Landau and Lifshitz, 1977), for $eE_{||}>0$,

$$\psi_{||}(Z)=N\,\mathrm{Ai}(\xi)\ , \tag{2.51}$$

with N a normalization constant, $\mathrm{Ai}(\xi)$ an Airy function (Abramowitz and Stegun, 1964), and

$$\xi=-(2MeE_{||}/\hbar^2)^{1/2}(Z+\mathscr{E}/eE_{||})\ . \tag{2.52}$$

The second solution[4] is of plane-wave time-dependent form and is an eigenfunction of the time-dependent constant of the motion $\mathscr{K}_z=P_z-eE_{||}t$ in Eq. (2.12). Noting that

$$\left[-i\hbar\frac{\partial}{\partial Z}-eE_{||}t-\hbar K_z\right]\exp\left[\frac{iZ}{\hbar}(\hbar K_z+eE_{||}t)\right]=0\ , \tag{2.53}$$

one can easily verify that

$$\Psi_{||}(Z,t)=\exp\left[\frac{iZ}{\hbar}(\hbar K_z+eE_{||}t)-\frac{i}{2M\hbar}\int^t d\tau(\hbar K_z+eE_{||}\tau)^2\right] \tag{2.54}$$

is a solution of Eq. (2.50) as well as an eigenfunction of $\mathscr{K}_z$ with eigenvalue $\hbar K_z$.

2. Magnetic field

Time-independent wave functions for a charged particle in a magnetic field may be found in many places (Landau, 1930; Johnson and Lippmann, 1949; Landau and Lifshitz, 1977; Garstang, 1977).

The Hamiltonian $H_\perp^0$ has two constants of motion, $\mathscr{K}_x^0$ and $\mathscr{K}_y^0$ in Eq. (2.14). The commutation relations of these operators and Π_x and Π_y are

$$\begin{aligned}&[\Pi_x,\Pi_y]=-[\mathscr{K}_x^0,\mathscr{K}_y^0]=i\hbar M\omega=\frac{ie\hbar B}{c}\ ,\\ &[\Pi_\alpha,\mathscr{K}_\beta^0]=0\quad(\alpha,\beta=x,y)\ .\end{aligned} \tag{2.55}$$

Since the constants of motion do not commute, only one function of them can be diagonalized (Johnson and Lippmann, 1949). This means, in particular, that they cannot *both* be given the eigenvalue zero, which would correspond classically to choosing the center of the circular orbit as the origin of the coordinate system (see below).

One familiar class of solutions arises from diagonalizing $H_\perp^0$ and *either* $\mathscr{K}_x^0$ or $\mathscr{K}_y^0$ (which then has the eigenvalue $\hbar K_x$ or $\hbar K_y$, respectively). If $\mathscr{K}_x^0$ is diagonal, the eigenfunction is

$$\psi_{\perp;nK_x}=\exp[iX(K_x+M\omega Y/2\hbar)]\chi_{\perp,nK_x}(Y)\ , \tag{2.56}$$

where

$$\chi_{\perp;nK_x}(Y)=(\lambda\sqrt{\pi}2^n n!)^{-1/2}\exp\left[-\frac{1}{2\lambda^2}(Y-Y_c)^2\right]\times H_n\left[\frac{1}{\lambda}(Y-Y_c)\right]\ . \tag{2.57}$$

If $\mathscr{K}_y^0$ is diagonal, then

$$\psi_{\perp;nK_y}=\exp[iY(K_y-M\omega X/2\hbar)]\chi_{\perp;nK_y}(X)\ , \tag{2.58}$$

where

$$\chi_{\perp;nK_y}(X)=(\lambda\sqrt{\pi}2^n n!)^{-1/2}\exp\left[-\frac{1}{2\lambda^2}(X-X_c)^2\right]\times H_n\left[\frac{1}{\lambda}(X-X_c)\right]\ . \tag{2.59}$$

Here $H_n(\xi)$ is an Hermite polynomial (Gradshteyn and Ryzhik, 1965) and λ is the first cyclotron radius (the root-mean-square radius in the orbit of lowest energy)

$$\lambda=[\hbar c/|e|B]^{1/2}=[\hbar/M|\omega|]^{1/2}\ . \tag{2.60}$$

The coordinates X_c and Y_c refer to the center of the classical orbit [compare with Eq. (2.17)]

$$\begin{aligned}X_c&=\hbar K_y/M\omega\ ,\\ Y_c&=-\hbar K_x/M\omega\ .\end{aligned} \tag{2.61}$$

The nth energy eigenvalue, corresponding to either $\psi_{\perp;nK_x}$ or $\psi_{\perp;nK_y}$, is

$$\mathscr{E}_{\perp n}=\hbar|\omega|(n+\tfrac{1}{2})\ , \tag{2.62}$$

which is independent of the value of K_x or K_y, respectively. This is known as the *Landau degeneracy*. These solutions are usually obtained by transforming initially to one or the other of the unsymmetric gauges (Landau and Lifshitz, 1977), $\underline{A}=-BY\underline{\hat{x}}$ or $\underline{A}=BX\underline{\hat{y}}$. The most general solution in this class diagonalizes an arbitrary linear combination of $\mathscr{K}_x^0$ and $\mathscr{K}_y^0$, and corresponds classically to fixing the center of the orbit to lie on a line passing through the origin.

The other common class of solutions, called the *angular momentum basis* here, results from diagonalizing $(\mathscr{K}_x^0)^2+(\mathscr{K}_y^0)^2$. Equation (2.18) states that this corresponds to giving a definite value to R_c, the distance of the center of the classical orbit from the origin. Since these solutions will be used in Sec. V, we shall go into a bit

[4] We have not found any specific reference to this solution and are not sure of its origin. It is, however, included in a more general set of solutions given by Bergou (1980).

more detail.

It is convenient to work with the dimensionless complex coordinates

$$W=(X+i\sigma Y)/\sqrt{2}\lambda$$

and

$$W^*=(X-i\sigma Y)/\sqrt{2}\lambda\ , \tag{2.63}$$

where σ is ± 1, depending on the sign of the charge,

$$\sigma=\mathrm{sgn}(e)\ . \tag{2.64}$$

Also, instead of the operators Π_x, Π_y, $\mathscr{K}_x^0$, and $\mathscr{K}_y^0$, we shall follow Malkin and Man'ko (1968) and Avron, Herbst, and Simon (1978) and use

$$\begin{aligned}
a&=i\lambda(\Pi_x+i\sigma\Pi_y)/\sqrt{2}\hbar=\frac{\partial}{\partial W^*}+\frac{1}{2}W\ ,\\
a^\dagger&=-i\lambda(\Pi_x-i\sigma\Pi_y)/\sqrt{2}\hbar=-\frac{\partial}{\partial W}+\frac{1}{2}W^*\ ,\\
b&=i\lambda(\mathscr{K}_x^0-i\sigma\mathscr{K}_y^0)/\sqrt{2}\hbar=\frac{\partial}{\partial W}+\frac{1}{2}W^*\ ,\\
b^\dagger&=-i\lambda(\mathscr{K}_x^0+i\sigma\mathscr{K}_y^0)/\sqrt{2}\hbar=-\frac{\partial}{\partial W^*}+\frac{1}{2}W\ .
\end{aligned} \tag{2.65}$$

These have the commutation relations

$$\begin{aligned}
&[a^\dagger,a]=[b^\dagger,b]=1\ ,\\
&[a,b]=[a,b^\dagger]=[a^\dagger,b]=[a^\dagger,b^\dagger]=0\ ,
\end{aligned} \tag{2.66}$$

and consequently comprise annihilation and creation operators for two one-dimensional harmonic oscillators (Messiah, 1961).

The Hamiltonian can now be expressed as

$$\begin{aligned}
H_\perp^0&=\frac{1}{2M}(\Pi_x^2+\Pi_y^2)\\
&=\hbar\,|\,\omega\,|\,(a^\dagger a+\tfrac{1}{2})\ ,
\end{aligned} \tag{2.67}$$

which is independent of b and $b^\dagger$. The name "angular momentum basis" stems from the fact that the z component of the canonical angular momentum takes the form

$$\begin{aligned}
L_z&=XP_y-YP_x\\
&=\frac{1}{2M\omega}[(\mathscr{K}_x^0)^2+(\mathscr{K}_y^0)^2-\Pi_x^2-\Pi_y^2]\\
&=\sigma\hbar(b^\dagger b-a^\dagger a)\ .
\end{aligned} \tag{2.68}$$

Thus, if $\psi_\perp$ is an eigenfunction of both the number operators $a^\dagger a$ and $b^\dagger b$, it is a simultaneous eigenfunction of $H_\perp^0$ and L_z.

The wave functions

$$\psi_{\perp;n_1n_2}(W,W^*),\quad n_i=0,1,2,\ldots,$$

are chosen to satisfy the equations

$$\begin{aligned}
a\psi_{\perp;n_1n_2}&=(n_1)^{1/2}\psi_{\perp;n_1-1,n_2}\ ,\\
a^\dagger\psi_{\perp;n_1n_2}&=(n_1+1)^{1/2}\psi_{\perp;n_1+1,n_2}\ ,\\
b\psi_{\perp;n_1n_2}&=(n_2)^{1/2}\psi_{\perp;n_1,n_2-1}\ ,\\
b^\dagger\psi_{\perp;n_1n_2}&=(n_2+1)^{1/2}\psi_{\perp;n_1,n_2+1}\ .
\end{aligned} \tag{2.69}$$

Consequently,

$$\begin{aligned}
(a^\dagger a-n_1)\psi_{\perp;n_1n_2}&=0\ ,\\
(b^\dagger b-n_2)\psi_{\perp;n_1n_2}&=0\ ,
\end{aligned} \tag{2.70}$$

and the eigenvalues of $H_\perp^0$ and L_z are $\mathscr{E}_{\perp n_1}$ and $m\hbar$, respectively, where

$$\mathscr{E}_{\perp n_1}=\hbar\,|\,\omega\,|\,(n_1+\tfrac{1}{2})\ , \tag{2.71}$$

and

$$m=\sigma(n_2-n_1)\ . \tag{2.72}$$

The state $\psi_{\perp;00}$ (normalized in X and Y) can be obtained from the fact that it is annihilated by either a or b:

$$\psi_{\perp;00}=\frac{1}{\sqrt{2\pi}\lambda}\exp\left[-\frac{|\,W\,|^2}{2}\right]\ . \tag{2.73}$$

The general state is then found by, applying Eqs. (2.69) and a little work,

$$\begin{aligned}
\psi_{\perp;n_1n_2}&=[n_1!n_2!]^{-1/2}(a^\dagger)^{n_1}(b^\dagger)^{n_2}\psi_{\perp;00}\\
&=\begin{cases}
\dfrac{(-)^{n_1}}{\lambda}\left[\dfrac{n_1!}{2\pi n_2!}\right]^{1/2}W^{n_2-n_1}L_{n_1}^{n_2-n_1}(\,|\,W\,|^2)\exp(-\,|\,W\,|^2/2)\ , & n_2>n_1\\
\dfrac{(-)^{n_2}}{\lambda}\left[\dfrac{n_2!}{2\pi n_1!}\right]^{1/2}(W^*)^{n_1-n_2}L_{n_2}^{n_1-n_2}(\,|\,W\,|^2)\exp(-\,|\,W\,|^2/2)\ , & n_1>n_2
\end{cases}
\end{aligned} \tag{2.74}$$

where L_n^k is an associated Laguerre polynomial (Gradshteyn and Ryzhik, 1965). The two cases of Eq. (2.74) may be cast into the single form (Landau and Lifshitz, 1977)

$$\psi_{\perp;n_1n_2}=\frac{(-)^{n_r}}{\lambda}\left[\frac{n_r!}{2\pi(n_r+|\,m\,|)!}\right]^{1/2}e^{im\phi}\left[\frac{R_\perp^2}{2\lambda^2}\right]^{|\,m\,|/2}L_{n_r}^{|\,m\,|}\left[\frac{R_\perp^2}{2\lambda^2}\right]\exp\left[-\frac{R_\perp^2}{4\lambda^2}\right] \tag{2.75}$$

in terms of the cylindrical coordinates defined by

$$X=R_\perp\cos\phi,\quad Y=R_\perp\sin\phi\ . \tag{2.76}$$

The magnetic quantum number m has been defined in Eq. (2.72). The radial node number is

$$n_r=\min(n_1,n_2)=\tfrac{1}{2}(n_1+n_2-|\,n_1-n_2\,|)\ . \tag{2.77}$$

The inverse relations are

$$\begin{aligned} n_1&=n_r+\tfrac{1}{2}(|\,m\,|-\sigma m)\ ,\\ n_2&=n_r+\tfrac{1}{2}(|\,m\,|+\sigma m)\ . \end{aligned} \tag{2.78}$$

Thus, for a given n_r, the energy $\hbar|\,\omega\,|(n_1+\frac{1}{2})$ is infinitely degenerate for all $\sigma m>0$.

E. Wave functions with $E_\perp\neq 0$

The solutions for the Schrödinger equation for an observer in the lab frame ($E_\perp\neq 0$) can be obtained from the drift-frame ($E_\perp=0$) solutions of Sec. II.D. This can be accomplished by inverting the transformation U, which boosts from the lab to the drift frame. The lab Hamiltonian separates into

$$H=H_\perp+H_{||}\ , \tag{2.79}$$

with

$$H_\perp=\frac{1}{2M}(\Pi_x^2+\Pi_y^2)-eE_\perp Y\ , \tag{2.80}$$

and $H_{||}$ as in Eq. (2.49). The solution to the equation

$$\left[H_\perp-i\hbar\frac{\partial}{\partial t}\right]\Psi_\perp(X,Y,t)=0 \tag{2.81}$$

is obtained by the result from Sec. II.C that

$$H_{\perp U}=UH_\perp U^\dagger-i\hbar U\left[\frac{\partial}{\partial t}U^\dagger\right]=H_\perp^0\ , \tag{2.82}$$

where $H_\perp^0$ is given in Eq. (2.48) and is simply $H_\perp$ with $E_\perp=0$. The transformation U is obtained from Eqs. (2.34) and (2.41), with $\underline{v}=\underline{v}_d=\hat{\underline{x}}cE_\perp/B$,

$$U=\exp[-iv_d(MX-\mathscr{K}_x^0 t)/\hbar]\ , \tag{2.83}$$

where

$$\mathscr{K}_x^0=P_x-\frac{M\omega}{2}Y\ . \tag{2.84}$$

1. Eigenfunctions of $\mathscr{K}_x$

The wave functions in the drift frame might be, for instance,

$$\Psi_{\perp U}(X,Y,t)=\psi_{\perp;n}(X,Y)\exp(-i\mathscr{E}_{\perp n}t/\hbar)\ , \tag{2.85}$$

where $\psi_{\perp;n}$ is a generic symbol for any of the three time-independent eigenfunctions in Eqs. (2.56), (2.58), and (2.74). In the lab frame, the corresponding wave functions are therefore

$$\begin{aligned} \Psi_\perp&=U^\dagger\Psi_{\perp U}\\ &=\exp\left[\frac{iMv_dX}{\hbar}-\frac{iMv_d^2t}{2\hbar}\right]\exp\left[-\frac{iv_dt\mathscr{K}_x^0}{\hbar}\right]\Psi_{\perp U}\ , \end{aligned} \tag{2.86}$$

where Eq. (2.33) has been employed. Note that $\psi_{\perp;n\mathscr{K}_x}$, the eigenfunction of $\mathscr{K}_x^0$ as given by Eq. (2.56), is singled out. Application of the exponential operator converts $\mathscr{K}_x^0$ into the eigenvalue $\hbar K_x$, and all terms linear in t in the argument of the exponential then enter into the definition of the energy in the lab frame.[5] The end result is

$$\begin{aligned} \Psi_\perp(X,Y,t)=\exp&\left[iX\left[K_x+\frac{Mv_d}{\hbar}+\frac{M\omega Y}{2\hbar}\right]\right.\\ &\left.-i\frac{\mathscr{E}_{\perp l}t}{\hbar}\right]\chi_{\perp;nK_x}(Y)\ , \end{aligned} \tag{2.87}$$

where $\chi_{\perp;nK_x}$ appears in Eq. (2.57) and

$$\begin{aligned} \mathscr{E}_{\perp l}&=\mathscr{E}_{\perp n}+\hbar K_xv_d+\frac{Mv_d^2}{2}\\ &=\hbar|\,\omega\,|(n+\tfrac{1}{2})+\hbar K_xv_d+\frac{Mv_d^2}{2}\ . \end{aligned} \tag{2.88}$$

This should be compared with the classical result in Eq. (2.20). The Landau degeneracy associated with a charged particle in a magnetic field is broken in exactly the same way by the addition of a perpendicular electric field. Note that the wave function is now an eigenfunction of

$$\mathscr{K}_x=U^\dagger\mathscr{K}_x^0U=P_x-\frac{M\omega Y}{2}-Mv_d \tag{2.89}$$

with eigenvalue $\hbar K_x$.

The wave functions in Eq. (2.87) have been obtained before by working in the energy representation (e.g., Gol'dman *et al.*, 1960; Blumberg, Itano, and Larson, 1979). Just as for the free particle example of Eqs. (2.31) and (2.32), it is only the time-independent part $\exp(iMv_dX/\hbar)$ of $U^\dagger$ that is needed.[6] The somewhat more tortuous route followed here has the advantage of showing how the eigenfunctions of $\mathscr{K}_x^0$ are automatically selected if $\Psi_\perp$ in the lab frame is to be a stationary state.

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[5] More or less the same situation occurs when one switches to a coordinate system rotating uniformly around the axis of a constant magnetic field. If $\psi_m(\underline{R})$ is an eigenfunction of L_z with eigenvalue $m\hbar$, then application of $\exp(-i\alpha L_zt/\hbar)$ to $\psi_m(\underline{R})\exp(-i\mathscr{E}t/\hbar)$ merely changes $\mathscr{E}$ to $\mathscr{E}+\alpha\pi\hbar$. However, the transformation to rotating coordinates is very useful in either problems where the magnetic field itself is rotating (Series, 1978; Rabi, Ramsey, and Schwinger, 1954) or problems involving circularly polarized electromagnetic fields (Salzman, 1974).

[6] A closely related time-independent "boosting" procedure was used on the interparticle distance of a two-body system in crossed $\underline{E}$ and $\underline{B}$ by Burkova, Dzyaloshinskii, Drukarev, and Monozon (1976).

2. Other eigenfunctions

The wave function $\psi_{\perp;n}$ could just as well have been the eigenfunction of $\mathscr{K}_y^0$ in Eq. (2.58) or of $(\mathscr{K}_x^0)^2+(\mathscr{K}_y^0)^2$ in Eq. (2.74). In these cases, Eq. (2.86) reduces to

$$\Psi_\perp = \exp\left[\frac{iMv_dX}{\hbar}+\frac{ieE_\perp}{2\hbar}Yt-\frac{it}{\hbar}\left[\mathscr{E}_{\perp n}+\frac{Mv_d^2}{2}\right]\right]\psi_{\perp;n}(X-v_dt,Y)\ . \tag{2.90}$$

These are also perfectly valid solutions to Eq. (2.81). For the choice $\psi_{\perp;n}=\psi_{\perp;nK_y}$ of Eq. (2.58), this is

$$\Psi_\perp=\exp\left[\frac{iMv_d}{\hbar}X-\frac{it}{\hbar}\left[\mathscr{E}_{\perp n}+\frac{Mv_d^2}{2}\right]+\frac{i}{\hbar}Y\left[\hbar K_y-\frac{M\omega}{2}X+eE_\perp t\right]\right]\chi_{\perp;nK_y}(X-v_dt)\ , \tag{2.91}$$

where, from Eq. (2.59),

$$\chi_{\perp;nK_y}(X-v_dt)=(\lambda\sqrt{\pi}2^n n!)^{-1/2}\exp\left[-\frac{1}{2\lambda^2}(X-X_c-v_dt)^2\right]H_n\left[\frac{1}{\lambda}(X-X_c-v_dt)\right]\ . \tag{2.92}$$

The lab solution may obviously be identified as an eigenfunction of

$$\mathscr{K}_y=U^\dagger\mathscr{K}_y^0U=P_y+\frac{M\omega}{2}X-eE_\perp t\ . \tag{2.93}$$

Thus $\Psi_\perp$ here corresponds to a one-dimensional Gaussian centered about the X coordinate X_c+v_dt of the guiding center, with plane-wave nature in the Y coordinate.

For the other choice, $\psi_{\perp;n}=\psi_{\perp;n_1n_2}$ of Eq. (2.74) with $n=n_1$, the lab wave function is a two-dimensional Gaussian centered about the moving origin $(X,Y)=(v_dt,0)$. From the discussion of Sec. II.D.2, it is an eigenfunction

$$U^\dagger[(\mathscr{K}_x^0)^2+(\mathscr{K}_y^0)^2]U=\mathscr{K}_x^2+\mathscr{K}_y^2\ , \tag{2.94}$$

or, equivalently, of

$$\begin{aligned}U^\dagger L_zU&=U^\dagger(XP_y-YP_x)U\\&=(X-v_dt)\left[P_y-\frac{eE_\perp t}{2}\right]-Y(P_x-Mv_d)\ .\end{aligned} \tag{2.95}$$

These are constants of the motion which are explicitly time dependent for $E_\perp\neq0$. The one in Eq. (2.95) has the physical interpretation of corresponding to L_z in the drift frame. It was derived earlier in a different manner, and without the link to the drift frame, in Eq. (3.13) of Bacry, Combe, and Richard (1970b).

These examples are not the only ones in which the wave function follows a time-dependent path. There are more general solutions which can be described as following the classical path of the particle, and these are now obtained.

F. Solutions which follow a classical path

So far only inertially comoving frames have been considered. Nonrelativistically it is an easy matter to transform to a frame accelerating with respect to the laboratory (Amundsen, 1978; Greenberger, 1979). For quadratic Hamiltonians such as the harmonic oscillator, this underlies the fact that time-dependent Gaussian wave packets can be obtained which differ from the stationary states chiefly by the replacement of $\underline{R}$ by $\underline{R}-\underline{R}_{\rm cl}(t)$, where $\underline{R}_{\rm cl}(t)$ is a solution of the corresponding classical equations of motion (Schrödinger, 1926; Husimi, 1953; Senitzky, 1954; Kerner, 1958; Treanor, 1965; Heller, 1975).

A charged particle in constant fields is also an example having a quadratic Hamiltonian for which such wave packets can be obtained. To see this, consider the unitary transformation

$$\mathscr{U}=\exp(-iS/\hbar)\ , \tag{2.96}$$

$$S=M\dot{\underline{R}}_{\rm cl}(t)\cdot\underline{R}-\underline{R}_{\rm cl}(t)\cdot\underline{\mathscr{K}}^0+\frac{e}{2}\int^t\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\ , \tag{2.97}$$

where $\underline{R}_{\rm cl}$ is as yet unspecified. [If $\underline{R}_{\rm cl}=\underline{v}t$, S differs from $\underline{v}\cdot\underline{G}$ of Eq. (2.34) only by a purely time-dependent factor.] It is easily verified that $\mathscr{U}$ boosts along $\underline{R}_{\rm cl}(t)$:

$$\begin{aligned}\underline{R}_{\mathscr{U}}&=\mathscr{U}\underline{R}\mathscr{U}^\dagger=\underline{R}+\underline{R}_{\rm cl}\ ,\\ \underline{\Pi}_{\mathscr{U}}&=\mathscr{U}\underline{\Pi}\mathscr{U}^\dagger=\underline{\Pi}+M\dot{\underline{R}}_{\rm cl}\ .\end{aligned} \tag{2.98}$$

The Hamiltonian H in Eq. (2.3) is transformed to

$$H_{\mathscr{U}}=\frac{\Pi^2}{2M}+(\underline{R}+\tfrac{1}{2}\underline{R}_{\rm cl})\cdot\left[M\ddot{\underline{R}}_{\rm cl}-e\underline{E}-\frac{e}{c}\dot{\underline{R}}_{\rm cl}\times\underline{B}\right]\ . \tag{2.99}$$

If $\underline{R}_{\rm cl}$ is chosen to be the solution of the corresponding classical problem, the Lorentz force law then tells us that $H_{\mathscr{U}}=\Pi^2/2M$, which is *exactly* the same form as for a charged particle in constant $\underline{B}$. Accordingly, we hereafter take $\underline{R}_{\rm cl}$ to be given by Eqs. (2.15):

$$\begin{aligned}X_{\rm cl}&=\rho\sin(\omega t+\theta)+\frac{\hbar K_y}{M\omega}+v_dt\ ,\\ Y_{\rm cl}&=\rho\cos(\omega t+\theta)-\frac{\hbar K_x}{M\omega}\ ,\\ Z_{\rm cl}&=Z_0+\frac{\hbar K_z}{M}t+\frac{eE_{||}}{2M}t^2\ .\end{aligned} \tag{2.100}$$

From the relation

$$M\dot{\underline{R}}_{\rm cl}=\underline{P}_{\rm cl}-(e/2c)\underline{B}\times\underline{R}_{\rm cl}\ ,$$

it is seen that S in Eq. (2.97) may also be written as

$$S=\underline{P}_{\rm cl}\cdot\underline{R}-\underline{R}_{\rm cl}\cdot\underline{P}+\tfrac{1}{2}\int^t e\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\ . \tag{2.101}$$

Furthermore, S is a constant of the motion if $\underline{E}$ is identically zero.

By way of contrast with the inertial boost to the drift frame, *both* $\underline{E}_\perp$ and $\underline{E}_{||}$ have vanished from the Hamiltonian. Here $\underline{E}_{||}$ disappears because we have shifted to a frame uniformly accelerating in the z direction, so now the z motion has no component of acceleration. (This operation commutes with the X-Y transformation.)

Using Eqs. (2.33), (2.96), and (2.101),

$$\mathscr{U}^\dagger=\exp\left[\frac{i}{\hbar}\left[\underline{P}_{\rm cl}\cdot(\underline{R}-\tfrac{1}{2}\underline{R}_{\rm cl})+\tfrac{1}{2}\int^t e\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\right]\right]\exp\left[-\frac{i}{\hbar}\underline{R}_{\rm cl}\cdot\underline{P}\right]\ , \tag{2.102}$$

so that

$$\begin{aligned}\Psi(\underline{R},t)&=\mathscr{U}^\dagger\Psi_{\mathscr{U}}(\underline{R},t)\\&=\exp\left[\frac{i}{\hbar}(\underline{P}_{\rm cl}\cdot\underline{R}-\tfrac{1}{2}\underline{P}_{\rm cl}\cdot\underline{R}_{\rm cl}+\tfrac{1}{2}\int^t e\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\right]\Psi_{\mathscr{U}}(\underline{R}-\underline{R}_{\rm cl},t)\\&=\exp\left[\frac{i}{\hbar}[\underline{P}_{\rm cl}\cdot\underline{R}+F(t)]\right]\Psi_{\mathscr{U}}(\underline{R}-\underline{R}_{\rm cl},t)\ .\end{aligned} \tag{2.103}$$

Since

$$\hbar\underline{K}=\underline{P}_{\rm cl}+\frac{e}{2c}\underline{B}\times\underline{R}_{\rm cl}-e\underline{E}t\ , \tag{2.104}$$

the purely time-dependent factor $F(t)$ has an alternative form,

$$\begin{aligned}F(t)&=-\tfrac{1}{2}\underline{P}_{\rm cl}\cdot\underline{R}_{\rm cl}+\frac{e}{2}\int^t\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\\&=-\tfrac{1}{2}\hbar\underline{K}\cdot\underline{R}_{\rm cl}-\tfrac{1}{2}e\underline{E}\cdot\underline{R}_{\rm cl}t+\tfrac{1}{2}\int^t e\underline{E}\cdot\underline{R}_{\rm cl}(\tau)d\tau\\&=-\tfrac{1}{2}\hbar\underline{K}\cdot\underline{R}_{\rm cl}-\tfrac{1}{2}\int^t e\underline{E}\cdot\dot{\underline{R}}_{\rm cl}(\tau)\tau d\tau\\&=-\tfrac{1}{2}\int^t(\hbar\underline{K}+e\underline{E}\tau)\cdot\dot{\underline{R}}_{\rm cl}(\tau)d\tau\ ,\end{aligned} \tag{2.105}$$

where constants of integration from the indefinite integrals have been ignored.

So, factoring Ψ, $\Psi_{\mathscr{U}}$, and F into perpendicular and parallel components,

$$\Psi_\perp(X,Y,t)=\exp\left[\frac{i}{\hbar}(P_{{\rm cl},x}X+P_{{\rm cl},y}Y+F_\perp)\right]\Psi_{\perp\mathscr{U}}(X-X_{\rm cl},Y-Y_{\rm cl},t)\ , \tag{2.106}$$

$$\begin{aligned}\Psi_{||}(Z,t)&=\exp\left[\frac{i}{\hbar}(P_{{\rm cl},z}Z+F_{||})\right]\Psi_{||\mathscr{U}}(Z-Z_{\rm cl},t)\\&=\exp\left[\frac{i}{\hbar}Z(\hbar K_z+eE_{||}t)-\frac{i}{2M\hbar}\int^t(\hbar K_z+eE_{||}\tau)^2d\tau\right]\Psi_{||\mathscr{U}}(Z-Z_{\rm cl},t)\ .\end{aligned} \tag{2.107}$$

The last function has been explicitly expanded to make some connections.

(i) If $\Psi_{||\mathscr{U}}$ is just unity [a special case of the free-particle solution in Eq. (2.31)], then $\Psi_{||}(Z,t)$ reduces to the plane-wave type of electric field wave function given in Eq. (2.54);

(ii) If $\Psi_{||\mathscr{U}}$ is a free-particle Gaussian wave packet

$$\Psi_{||\mathscr{U}}(Z,t)=(2\pi)^{-1/4}(\beta/\alpha)^{1/2}\exp(-Z^2/4\alpha)\ , \tag{2.108}$$

then

$$\begin{aligned}\Psi_{||}(Z,t)=(2\pi)^{-1/4}(\beta/\alpha)^{1/2}&\times\exp\left[-\frac{(Z-Z_{\rm cl})^2}{4\alpha}\right.\\&\left.+\frac{i}{\hbar}Z(\hbar K_z+eE_{||}t)+\frac{i}{\hbar}F_{||}\right]\ .\end{aligned} \tag{2.109}$$

Here

$$\alpha=\beta^2+\frac{i\hbar t}{2M}\ , \tag{2.110}$$

and β is a measure of the initial localization of the packet. The spreading wave packet in Eq. (2.109) was derived long ago by Kennard (1927) and Darwin (1928).

The fact that example (i) identifies time-dependent electric field functions with the free-particle stationary states has an interesting counterpart which has been discussed in the recent literature (Berry and Balazs, 1979; Greenberger and Overhauser, 1979; Greenberger, 1980). We may turn the argument around and take $\Psi_{||}$ as a stationary state for a charged particle in an electric field [the Airy function of Eq. (2.51)]. The boost to a frame uniformly accelerating in the z direction still transforms the Hamiltonian $H_{||}$ into a free-particle Hamiltonian, but the boosted wave function is then

$$\begin{aligned}\Psi_{||\mathscr{U}}(Z,t)&=\exp\left[-\frac{i}{\hbar}\left[P_{\mathrm{cl},z}Z-Z_{\mathrm{cl}}P_z+\tfrac{1}{2}eE_{||}\int^t Z_{\mathrm{cl}}(\tau)d\tau\right]\right]\mathrm{Ai}\left[-\left[\frac{2MeE_{||}}{\hbar^2}\right]^{1/2}\left[Z+\frac{\mathscr{E}}{eE_{||}}\right]\right]e^{-i\mathscr{E}t/\hbar}\\&=\exp\left[-\frac{i}{\hbar}\left[P_{\mathrm{cl},z}Z+\tfrac{1}{2}P_{\mathrm{cl},z}Z_{\mathrm{cl}}+\tfrac{1}{2}eE_{||}\int^t Z_{\mathrm{cl}}(\tau)d\tau+\mathscr{E}t\right]\right]\mathrm{Ai}\left[-\left[\frac{2MeE_{||}}{\hbar^2}\right]^{1/2}\left[Z+Z_{\mathrm{cl}}+\frac{\mathscr{E}}{eE_{||}}\right]\right]\ .\end{aligned} \tag{2.111}$$

This is a time-dependent (uniformly accelerating and nonspreading) wave packet for a free particle. Berry and Balazs explain that this solution, like a plane wave, corresponds to an infinite number of particles (and is not square integrable). Accordingly, the fact that the argument of the Airy function does not involve the classical path of a *single* free particle does not constitute a violation of Ehrenfest's theorem.

Turning to $\Psi_{\perp}$, we see that the function $\Psi_{\perp\mathscr{U}}(X,Y,t)$ may be taken as $\exp(-i\mathscr{E}_{\perp n}t/\hbar)$ times any of the time-independent magnetic field wave functions in Eqs. (2.56), (2.58), and (2.74). Then $\Psi_{\perp}$ will be a coherent (nonspreading) Gaussian wave packet. For example, choosing the solution in Eq. (2.56) with $K_x=0=Y_c$,

$$\Psi_{\perp;n0\mathscr{U}}(X,Y,t)=\exp\left[\frac{iM\omega XY}{2\hbar}-\frac{i\mathscr{E}_{\perp n}t}{\hbar}\right]\chi_{\perp;n0}(Y)\ , \tag{2.112}$$

$$\chi_{\perp;n0}(Y)=(\lambda\sqrt{\pi}2^n n!)^{-1/2}\exp\left[-\frac{Y^2}{2\lambda^2}\right]H_n\left[\frac{Y}{\lambda}\right]\ . \tag{2.113}$$

Then Eq. (2.106) produces the time-dependent wave packet

$$\begin{aligned}\Psi_{\perp;n0}&=\mathscr{U}^{\dagger}\Psi_{\perp;n0\mathscr{U}}\\&=\exp\left[\frac{i}{\hbar}[P_{\mathrm{cl},x}X+P_{\mathrm{cl},y}Y+F_{\perp}+M\omega(X-X_{\mathrm{cl}})(Y-Y_{\mathrm{cl}})/2-\mathscr{E}_{\perp n}t]\right]\chi_{\perp;n0}(Y-Y_{\mathrm{cl}})\ .\end{aligned} \tag{2.114}$$

Similar results are obtained if either of the other types of magnetic field wave functions is chosen. Thus there is an infinite number of these packets in one-to-one correspondence with the stationary states. This is the analog of Senitzky's result for the one-dimensional harmonic oscillator.

If $\Psi_{\perp\mathscr{U}}$ is chosen to correspond to the state $n_1=0$, $n_2=0$ in the angular momentum basis of Eq. (2.74), the result is the nodeless wave packet that was also given by Kennard and Darwin. The nodeless packets are closely related to the *coherent states* of a charged particle in constant fields, which were derived by Malkin and Man'ko (1968). These authors also considered the case where $E_{\perp}$ and B are arbitrary functions of time (Malkin, Man'ko, and Trifonov, 1970; Malkin and Man'ko, 1970).

Another interesting result from the above analysis is the existence of a quadratic time-dependent constant of the motion. Just as for the boost to the drift frame, this boost along the classical path has eliminated $E_{\perp}$, so that $[L_z,H_{\mathscr{U}}]=0$. Therefore, the Hamiltonian in the lab frame has the constant of motion

$$\mathscr{U}^{\dagger}L_z\mathscr{U}=[(\underline{R}-\underline{R}_{\mathrm{cl}})\times(\underline{P}-\underline{P}_{\mathrm{cl}})]_z\ , \tag{2.115}$$

which is derived using Eq. (2.101). Upon expanding, this is [see Eqs. (2.100)]

$$\begin{aligned}\mathscr{U}^{\dagger}L_z\mathscr{U}&=(X-v_dt)(P_Y-\tfrac{1}{2}eE_{\perp}t)-Y(P_x-Mv_d)-\rho\sin(\omega t+\theta)\Pi_y+\rho\cos(\omega t+\theta)(\Pi_x-Mv_d)\\&\quad-\frac{\hbar}{M\omega}K_y\mathscr{X}_y-\frac{\hbar}{M\omega}K_x(\mathscr{X}_x-Mv_d)-\frac{M\omega}{2}\rho^2+\frac{\hbar^2}{2M\omega^2}(K_x^2+K_y^2)\ .\end{aligned} \tag{2.116}$$

The only component of this quantity which is not obviously conserved or which has not been previously discussed is

$$\cos(\omega t+\theta)(\Pi_x - Mv_d) - \sin(\omega t+\theta)\Pi_y \ . \tag{2.117}$$

That this is a constant of the motion is related to the fact that the motion is harmonic in the drift frame.

III. DYNAMICAL OPERATORS FOR N PARTICLES IN CONSTANT FIELDS

A. Hamiltonian and constants of motion

Several features of the single-particle analysis have extensions to an N-body system with translationally invariant interactions. In particular, although the pseudomomenta for the individual particles are no longer conserved, their sum (the total pseudomomentum) is still a constant of the motion (Carter, 1967; Avron, Herbst, and Simon, 1978). Diagonalization of its components corresponds to separation of center-of-mass (CM) degrees of freedom, a subject to which we return in the next section.

Our first task is to convert to CM and internal coordinates, after which we perform the Power-Zienau-Woolley (PZW) transformation to the multipolar gauge (Power and Zienau, 1959; Woolley, 1971; Babiker, Power, and Thirunamachandran, 1974; Power, 1978; Yang, Hirschfelder, and Johnson, 1981). The convenience of this has been demonstrated in the two-body case by Lamb (1952); Elliott and Loudon (1959, 1960); Gor'kov and Dzyaloshinskii (1967); Breitenberger (1968); Carter (1969); Grotch and Hegstrom (1971); Ryvkin (1975); Avron, Herbst, and Simon (1978); O'Connell (1979); Wunner and Herold (1979); Pavlov-Verevkin and Zhilinskii (1980); Wunner, Ruder, and Herold (1980, 1981a, 1981b); and Herold, Ruder, and Wunner (1981). The only explicit N-body version we have found appears in Weisenthal and de Graaf (1971) and Moss and Perry (1972) (see also Sutter, Guarnieri, and Dreizler, 1970), though it is contained as a special case in our work on more general fields (Yang, Hirschfelder, and Johnson, 1981).

In this section, the previous treatments will be generalized by considering the operators of an N-particle system of arbitrary overall charge in *both* constant $\underline{E}$ and $\underline{B}$. In previous papers, at least as far as we know, an electric field has been included only in the neutral two-body case (Gor'kov and Dzyaloshinskii, 1967). However, a neutral system is somewhat special because its total pseudomomentum (which is generally time dependent) is time independent in the static symmetric gauge of Eqs. (2.5).

The Hamiltonian for N particles in the external fields is

$$H_{\rm tot} = H_{\rm mc} + H_{\rm spin} \ , \tag{3.1}$$

where $H_{\rm mc}$ is the minimally coupled orbital Hamiltonian and $H_{\rm spin}$ is a sum of terms of the form of Eq. (2.2),

$$H_{\rm spin} = \sum_{i=1}^{N} \frac{g_i e_i}{2m_i c} \underline{B}\cdot\underline{s}_i \ . \tag{3.2}$$

Particle i has mass m_i, charge e_i, gyromagnetic factor g_i, and spin $\underline{s}_i$. As in Sec. II, the spin can be quantized along $\underline{B}$, providing only constant terms to the energy. The difference here is that the wave functions for many particles may have to be totally symmetric or antisymmetric in some of the particles in accord with the Pauli exclusion principle. All of the operations we shall perform are totally symmetric to exchange of identical particles, however, so that permutational properties of the wave functions are not affected. Thus hereafter it will be sufficient for our purposes to neglect spin.

The orbital Hamiltonian is

$$H_{\rm mc} = \sum_{i=1}^{N} \left[\frac{\pi_i^2}{2m_i} - e_i \underline{E}\cdot\underline{r}_i \right] + V \ , \tag{3.3}$$

where $\underline{\pi}_i$ is the mechanical momentum of particle i,

$$\underline{\pi}_i = m_i \dot{\underline{r}}_i = \underline{p}_i - \frac{e_i}{c}\underline{A}_i = \underline{p}_i - \frac{e_i}{2c}\underline{B}\times\underline{r}_i \ , \tag{3.4}$$

$\underline{p}_i = -i\hbar\nabla_i$, and V is a translationally invariant sum of interaction potentials, as in the many-particle Coulomb interaction. Using Maxwell's equations, we find the equations of motion for $\underline{r}_i$ to be

$$m_i \ddot{\underline{r}}_i = e_i \underline{E} + \frac{e_i}{c}\dot{\underline{r}}_i \times \underline{B} - \nabla_i V \ . \tag{3.5}$$

Summing this over i,

$$M\ddot{\underline{R}} = e\underline{E} + \frac{e}{c}\dot{\underline{R}}\times\underline{B} + \frac{1}{c}\dot{\underline{\mu}}\times\underline{B} \ , \tag{3.6}$$

where the contributions from V have canceled and we have introduced the CM, the total mass, the total charge, and the dipole moment measured from the CM, namely,

$$\underline{R} = \sum_{i=1}^{N} \frac{m_i}{M}\underline{r}_i \ , \tag{3.7}$$

$$M = \sum_{i=1}^{N} m_i \ , \tag{3.8}$$

$$e = \sum_{i=1}^{N} e_i \ , \tag{3.9}$$

$$\underline{\mu} = \sum_{i=1}^{N} e_i(\underline{r}_i - \underline{R}) \ . \tag{3.10}$$

Frequent reference will also be made to the total canonical and mechanical momenta

$$\underline{P} = \sum_{i=1}^{N} \underline{p}_i = -i\hbar \sum_{i=1}^{N} \nabla_i \ , \tag{3.11}$$

$$\underline{\Pi}_{\rm mc} = M\dot{\underline{R}} = \sum_{i=1}^{N} \left[\underline{p}_i - \frac{e_i}{c}\underline{A}_i \right]$$

$$= \underline{P} - \frac{e}{2c}\underline{B}\times\underline{R} - \frac{1}{2c}\underline{B}\times\underline{\mu} \ . \tag{3.12}$$

[Note that $\underline{P}$ is *defined* by Eq. (3.11), independent of the gauge.] The symbols from the single-particle treatment are being employed for the CM quantities to accent

correspondences.

Equation (3.6) may now be written as [see Eqs. (2.8) and (2.9)]

$$\frac{d}{dt}\underline{\mathscr{K}}_{\rm mc}=0\ , \tag{3.13}$$

where

$$\underline{\mathscr{K}}_{\rm mc}=\underline{\Pi}_{\rm mc}+\frac{e}{c}\underline{B}\times\underline{R}+\frac{1}{c}\underline{B}\times\underline{\mu}-e\underline{E}t-M\underline{v}_d$$

$$=\underline{P}+\frac{e}{2c}\underline{B}\times\underline{R}+\frac{1}{2c}\underline{B}\times\underline{\mu}-e\underline{E}t-M\underline{v}_d\ . \tag{3.14}$$

Thus the total pseudomomentum $\underline{\mathscr{K}}_{\rm mc}$ is a constant of the motion. It is also the sum of the individual particle pseudomomenta, as mentioned above. The quantities $\underline{\Pi}_{\rm mc}$ and $\underline{\mathscr{K}}_{\rm mc}$ are seen to differ by only the dipole moment terms from their single-particle analogs in Eqs. (2.4) and (2.9), respectively, and to have the same commutation relations. The dipole moment $\underline{\mu}$ is a function of the $3N-3$ coordinates orthogonal to the CM, as discussed in the next subsection (III.B).

As a result of Eqs. (3.6) and (3.12) it is shown in Appendix A that the maximum deflection of a classical CM trajectory due to coupling with the internal motions (via $\underline{\mu}$) is extremely small and would be difficult to observe.

The constancy of the total pseudomomentum for N bodies in a pure magnetic field was shown by Avron, Herbst, and Simon (1978). [Carter (1967) shows this for neutral systems in an unpublished report.] Herold, Runner, and Wunner (1981) have further shown how this constant may be obtained when working in an arbitrary gauge for the vector potential instead of choosing a specific one from the outset. In this connection, $\underline{\mathscr{K}}_{\rm mc}$ (with the electric field included) is given in any gauge by the first line of Eq. (3.14), where $\underline{\Pi}_{\rm mc}$ is then $\underline{P}-\sum e_i\underline{A}_i/c$.

The z component of the total pseudomomentum can be associated with the initial z velocity of the CM, as for the single classical particle in Eq. (2.15). The physical interpretation of the x and y components becomes a bit more obscure than for the single-particle pseudomomentum, as mentioned by Grotch and Hegstrom (1971). *In the limit that the fields vanish* (letting $E_\perp$ go to zero before B),

$$\underline{\mathscr{K}}_{\perp\rm mc}=\underline{P}_\perp=M\dot{\underline{R}}_\perp\ , \tag{3.15}$$

and the total transverse pseudomomentum is simply the usual transverse momentum associated with the CM. On the other hand, *in the limit that the particle interactions vanish,* each particle performs an orbit as described in Sec. II.B. Then, using Eq. (2.18), $\underline{\mathscr{K}}_{\perp\rm mc}$ is classically

$$\underline{\mathscr{K}}_{\perp\rm mc}=\sum_{i=1}^{N}\left[\underline{p}_{i\perp}+\frac{e_i}{2c}\underline{B}\times\underline{r}_{i\perp}-e_i\underline{E}_\perp t-m_i\underline{v}_d\right]$$

$$=\sum_{i=1}^{N}\left[m_i(\dot{\underline{r}}_{i\perp}-\underline{v}_d)+\frac{e_i}{c}\underline{B}\times(\underline{r}_{i\perp}-\underline{v}_d t)\right]$$

$$=\sum_{i=1}^{N}\frac{e_i}{c}\underline{B}\times\underline{r}_{ic}\ , \tag{3.16}$$

where $\underline{r}_{ic}$ is the two-dimensional vector corresponding to the center of the circular orbit of particle i as viewed from the drift frame. Thus, in this limit, $\underline{\mathscr{K}}_{\perp\rm mc}$ is related to the charge centroid of the guiding centers (Carter, 1969b). *In intermediate regimes,* where the interaction potentials and the fields are both important, there appears to be no correspondingly simple interpretation. (See Sec. IV.B, where an informative solvable problem is discussed.)

When $E_\perp=0$, and V has rotational symmetry, there is another constant of the motion for this Hamiltonian, the z component of the total canonical angular momentum

$$L_{tz}=\sum_{i=1}^{N}[\underline{r}_i\times\underline{p}_i]_z$$

$$=[\underline{R}\times\underline{P}]_z+\sum_{i=1}^{N}\left[(\underline{r}_i-\underline{R})\times\left[\underline{p}_i-\frac{m_i}{M}\underline{P}\right]\right]_z$$

$$=L_{sz}+L_{rz}\ . \tag{3.17}$$

When $B=0$ as well as $E_\perp$, then L_{sz} and L_{rz} are separately conserved and mutually commuting. The term L_{sz} then has the interpretation of the component of the orbital angular momentum (about the origin) of a single particle of mass M at the position of the CM. The term L_{rz} represents the component of the total angular momentum relative to the CM. If $B\neq0$, they are not conserved individually, but their *sum* is conserved. We shall return to this operator at the end of this section and in Sec. IV.B. (Note that L_{sz} is not to be confused with a spin angular momentum.)

B. CM and internal variables—general linear diagonalizing coordinates

In order to treat the CM as an independent variable, a nonsingular transformation must be made from the spatial variables $\underline{r}_i$ to a new set $\underline{R}_i$ (with conjugate canonical momenta $\underline{p}_i$ and $\underline{P}_i$, respectively),[7]

$$\underline{R}_i=\sum_{j=1}^{N}D_{ij}\underline{r}_j\ , \tag{3.18}$$

$$\underline{P}_i=\sum_{j=1}^{N}(\underline{\underline{D}}^{-1T})_{ij}\underline{p}_j\ , \tag{3.19}$$

where the second equation follows from the first by the chain rule. We require that $\underline{R}_N\equiv\underline{R}$, the CM, which fixes $\underline{P}_N=\underline{P}$, the total canonical momentum.

In the following, we shall use the *general linear diagonalizing* (GLD) coordinates discussed in Yang, Hirschfelder, and Johnson (1981). For the GLD coordinates (related to "mass-weighted" or "mass-scaled" coordinates), the matrix $\underline{\underline{D}}$ takes the form

[7]Although it is possible to use redundant coordinates where the $3N$ internal coordinates are measured from the CM, we choose not to do so to avoid constraints on the variables.

$$\underline{\underline{D}}=\underline{\underline{a}}^{-1/2}\underline{\underline{d}}\,\underline{\underline{m}}^{1/2}\ , \tag{3.20}$$

where $\underline{\underline{a}}$ and $\underline{\underline{m}}$ are diagonal matrices with the non-negative elements

$$a_{ij}=a_i\delta_{ij},\quad m_{ij}=m_i\delta_{ij}\ , \tag{3.21}$$

and $\underline{\underline{d}}$ is an $N\times N$ orthogonal matrix (so that $\underline{\underline{d}}^{-1T}=\underline{\underline{d}}$) which can be characterized by $N(N-1)/2$ parameters.

The quantities a_i enter as arbitrary scale factors for the new coordinates, playing the role of reduced masses, with the exception of a_N; the requirement that $\underline{R}_N$ be the CM fixes a_N, d_{Ni} and, consequently, $(\underline{\underline{D}}^{-1T})_{Ni}$, so that

$$a_N=M,\quad d_{Ni}=[m_i/M]^{1/2},\quad (\underline{\underline{D}}^{-1T})_{Ni}=1\ . \tag{3.22}$$

There still remain $(N-1)(N-2)/2$ arbitrary parameters in $\underline{\underline{d}}$ which can be chosen to produce various sets of internal coordinates $\underline{R}_1\cdots\underline{R}_{N-1}$, e.g., Jacobi, mobile, or ones maintaining certain permutational symmetries (Radau, 1868; Hirschfelder and Dahler, 1956; Jepsen and Hirschfelder, 1959; Hirschfelder, 1969; Adamov and Natanson, 1970; Smith, 1980). (In normal modes problems, they are chosen to diagonalize the potential energy.) Since the best set of internal coordinates ultimately depends upon the particular system under consideration (for instance, atomic or molecular), there is no point in further specifying the matrix $\underline{\underline{d}}$. Merely by virtue of the fact that $\underline{\underline{d}}$ is orthogonal, there are no cross terms in the canonical momenta, and this is one of the reasons for our choice. It may be convenient in some cases to use internal coordinates which do exhibit such terms, but they will be linear combinations of the present $\underline{R}_1\cdots\underline{R}_{N-1}$, and so no generality is lost.

To re-express $H_{\rm mc}$ in terms of the $\underline{R}_i$, it will be helpful to couch $\underline{\dot{R}}_i$ in terms of the new canonical variables. From Eqs. (3.18)—(3.20), for all i including $i=N$,

$$\begin{aligned}\underline{\dot{R}}_i&=\sum_{k=1}^{N}D_{ik}\underline{\dot{r}}_k=\sum_{k=1}^{N}D_{ik}\frac{1}{m_k}\left[\underline{p}_k-\frac{e_k}{2c}\underline{B}\times\underline{r}_k\right]\\&=\frac{1}{a_i}\left[\underline{P}_i-\sum_{k=1}^{N}(\underline{\underline{D}}^{-1T})_{ik}\frac{e_k}{2c}\underline{B}\times\underline{r}_k\right]\\&=\frac{1}{a_i}\left[\underline{P}_i-\sum_{j=1}^{N}\frac{\varepsilon_{ij}}{2c}\underline{B}\times\underline{R}_j\right]\ .\end{aligned} \tag{3.23}$$

(Properly speaking, $\underline{\dot{R}}_i$ should be subscripted to denote the representation, but this is suppressed for notational convenience.) Here $\underline{\underline{\varepsilon}}$ is sort of an "effective charge" matrix

$$\begin{aligned}\varepsilon_{ij}&=\sum_{k=1}^{N}(\underline{\underline{D}}^{-1T})_{ik}e_k(\underline{\underline{D}}^{-1})_{kj}\\&=(a_ia_j)^{1/2}\sum_{k=1}^{N}\frac{e}{m_k}d_{ik}d_{jk}\ .\end{aligned} \tag{3.24}$$

It is symmetric and has, using Eq. (3.22), the total charge for its (N,N) element,

$$\varepsilon_{NN}=e\ . \tag{3.25}$$

Furthermore, it is straightforward to show by Eqs. (3.9), (3.10), (3.18), (3.22), and (3.24) that the dipole moment operator is defined in terms of $\varepsilon_{iN}=\varepsilon_{Ni}$ and the $N-1$ internal variables,

$$\begin{aligned}\underline{\mu}&=\sum_{j=1}^{N}e_j(\underline{r}_j-\underline{R})=\sum_{j=1}^{N}e_j\sum_{i=1}^{N-1}(\underline{\underline{D}}^{-1})_{ji}\underline{R}_i\\&=\sum_{i=1}^{N-1}\underline{R}_i\sum_{j=1}^{N}(\underline{\underline{D}}^{-1T})_{Nj}e_j(\underline{\underline{D}}^{-1})_{ji}\\&=\sum_{i=1}^{N-1}\varepsilon_{Ni}\underline{R}_i\ .\end{aligned} \tag{3.26}$$

(Another possible choice for the elements of $\underline{\underline{d}}$ is to make the dipole moment proportional to a single internal vector, e.g., $\underline{R}_{N-1}$. This amounts to requiring that $\varepsilon_{Ni}=0$ for $i\le N-2$.) Setting $i=N$ in Eq. (3.23) and employing Eqs. (3.22), (3.25), and (3.26) yields

$$\underline{\Pi}_{\rm mc}=M\underline{\dot{R}}=\underline{P}-\frac{e}{2c}\underline{B}\times\underline{R}-\frac{1}{2c}\underline{B}\times\underline{\mu}\ , \tag{3.27}$$

which correctly reproduces Eq. (3.12).

One of the convenient features of the GLD coordinates mentioned earlier is that there are no mass polarization terms. Actually, various quadratic quantities retain their diagonal form when expressed in terms of the new variables,

$$\sum_{i=1}^{N}m_i\dot{\underline{r}}_i^{\,2}=\sum_{i=1}^{N}m_i(\dot{\underline{r}}_i-\dot{\underline{R}}_N)^2+M\dot{\underline{R}}_N^{\,2}=\sum_{i=1}^{N}a_i\dot{\underline{R}}_i^{\,2}\ , \tag{3.28}$$

$$\sum_{i=1}^{N}\frac{p_i^2}{m_i}=\sum_{i=1}^{N}\frac{P_i^2}{a_i}\ , \tag{3.29}$$

$$\sum_{i=1}^{N}\underline{r}_i\times\underline{p}_i=\sum_{i=1}^{N}\underline{R}_i\times\underline{P}_i\ , \tag{3.30}$$

$$\sum_{i=1}^{N}m_ix_iy_i=\sum_{i=1}^{N}a_iX_iY_i\ . \tag{3.31}$$

Note that the first two of these identities are not equivalent when there is a nonzero vector potential. By using Eqs. (3.4), (3.9), (3.10), and (3.28), we can write $H_{\rm mc}$ of Eq. (3.3) as

$$\begin{aligned}H_{\rm mc}&=\sum_{i=1}^{N}(\tfrac{1}{2}m_i\dot{\underline{r}}_i^{\,2}-e_i\underline{E}\cdot\underline{r}_i)+V\\&=\sum_{i=1}^{N}\frac{1}{2}a_i\dot{\underline{R}}_i^{\,2}-e\underline{E}\cdot\underline{R}-\underline{\mu}\cdot\underline{E}+V\\&=\frac{\Pi_{\rm mc}^2}{2M}-e\underline{E}\cdot\underline{R}+T_{r,\rm mc}-\underline{\mu}\cdot\underline{E}+V\ ,\end{aligned} \tag{3.32}$$

where $\Pi_{\rm mc}^2/2M$ is the kinetic energy of the CM and $T_{r,\rm cm}$ is the kinetic energy of relative motion

$$T_{r,\rm mc}=\sum_{i=1}^{N-1}\frac{a_i}{2}\dot{\underline{R}}_i^{\,2}=\sum_{i=1}^{N-1}\frac{1}{2a_i}\left[\underline{P}_i-\sum_{j=1}^{N}\frac{\varepsilon_{ij}}{2c}\underline{B}\times\underline{R}_j\right]^2\ . \tag{3.33}$$

It is thus seen that, expressed in terms of the canonical variables, the relative kinetic energy contains the coordinates $\underline{R}_N=\underline{R}$ of the CM, while the CM kinetic energy contains the internal coordinates in the form of the dipole moment. The fact that there is coupling in both places is an inconvenience in calculations dealing with the CM. Notice from Eq. (3.23), however, that the coefficients of $\underline{R}_i$ in $\dot{\underline{R}}_N$ *and* of $\underline{R}_N$ in $\dot{\underline{R}}_i$ are the same, that is, ε_{iN}. The PZW transformation, to be described in III.C, takes advantage of this fact to eliminate $\underline{R}_N$ from the relative kinetic energy.

We have restricted the change of variables to Cartesian coordinates, since this is sufficient for our purposes. However, an area worth future study, which goes beyond the Cartesian coordinates, is the separation (or nonseparation) of the rotational coordinates of the N-particle system (Hirschfelder and Wigner, 1935; Curtiss, Hirschfelder, and Adler, 1950; Curtiss, 1953) from the multipolar Hamiltonian. Moss and Perry (1972) have examined some aspects of the related problem with molecular rotational coordinates based upon the nuclear inertia tensor. (They convert to the translational, rotational, vibrational, and electronic coordinates employed in Born-Oppenheimer-type applications.)

C. The Power-Zienau-Woolley transformation

The coupling of the kinetic energy operators can be reduced using the PZW transformation to the multipolar gauge, which is accomplished by the unitary operator

$$U_{\mathrm{PZW}}=\exp\left[-\frac{i}{2\hbar c}\underline{B}\cdot\underline{R}\times\underline{\mu}\right]$$
$$=\exp\left[-\frac{i}{2\hbar c}\underline{B}\times\underline{R}\cdot\sum_{j=1}^{N-1}\varepsilon_{Nj}\underline{R}_j\right]. \tag{3.34}$$

For $N=2$, $\underline{\mu}$ in Eq. (3.10) becomes

$$\underline{\mu}=e_1(\underline{r}_1-\underline{R})+e_2(\underline{r}_2-\underline{R})=\frac{e_1m_2-e_2m_1}{M}(\underline{r}_1-\underline{r}_2)\,, \tag{3.35}$$

and U_{PZW} simply

$$U_{\mathrm{PZW}}=\exp\left[-\frac{i}{2\hbar Mc}(e_1m_2-e_2m_1)\underline{B}\cdot\underline{R}\times(\underline{r}_1-\underline{r}_2)\right]. \tag{3.36}$$

This is the unitary transformation given by Lamb (1952) for the neutral case and by Grotch and Hegstrom (1971) for arbitrary e.

From Eqs. (3.14) and (3.12) and U_{PZW} in Eq. (3.34), the operators representing the pseudomomentum and the mechanical momentum in the multipolar gauge are, respectively,

$$\underline{\mathscr{K}}_{\mathrm{mp}}=U_{\mathrm{PZW}}\underline{\mathscr{K}}_{\mathrm{mc}}U_{\mathrm{PZW}}^{\dagger}=\underline{P}+\frac{e}{2c}\underline{B}\times\underline{R}-e\underline{E}t-M\underline{v}_d \tag{3.37}$$

and

$$\underline{\Pi}_{\mathrm{mp}}=U_{\mathrm{PZW}}\underline{\Pi}_{\mathrm{mc}}U_{\mathrm{PZW}}^{\dagger}=\underline{P}-\frac{e}{2c}\underline{B}\times\underline{r}-\frac{1}{c}\underline{B}\times\underline{\mu}\,. \tag{3.38}$$

The dipole moment term has been eliminated from the pseudomomentum, while it has been doubled in the operator $\underline{\Pi}_{\mathrm{mp}}$ representing $M\dot{\underline{R}}$. [In line with the remark after Eq. (3.12), the definition of $\underline{P}$ as a differential operator is independent of gauge, but its relationship with the physically meaningful velocity, is not.] The operator for the CM kinetic energy is thus transformed from $\Pi_{\mathrm{mc}}^2/2M$ to $\Pi_{\mathrm{mp}}^2/2M$.

The only other part of H_{mc} affected by the PZW transformation is the internal kinetic energy $T_{r,\mathrm{mc}}$ in Eq. (3.33),

$$T_{r,\mathrm{mp}}=U_{\mathrm{PZW}}T_{r,\mathrm{mc}}U_{\mathrm{PZW}}^{\dagger}$$
$$=\sum_{i=1}^{N-1}\frac{1}{2a_i}\left[\underline{P}_i-\sum_{j=1}^{N-1}\frac{\varepsilon_{ij}}{2c}\underline{B}\times\underline{R}_j\right]^2. \tag{3.39}$$

Note that $\underline{R}$ no longer appears here, since the sum over j only runs up to $N-1$. Thus the internal kinetic energy operator is explicitly independent of the CM in the new representation.

The final form for the Hamiltonian is, dropping the subscript *mp* hereafter,

$$H=U_{\mathrm{PZW}}H_{\mathrm{mc}}U_{\mathrm{PZW}}^{\dagger}=\frac{\Pi^2}{2M}-e\underline{E}\cdot\underline{R}+T_r-\underline{\mu}\cdot\underline{E}+V\,, \tag{3.40}$$

and the *only* coupling between the CM and internal coordinates is due to the appearance of the dipole moment in $\underline{\Pi}_{\mathrm{mp}}=\underline{\Pi}$. Furthermore, comparison of Eqs. (2.9) and (3.37) shows that the pseudomomentum $\underline{\mathscr{K}}_{\mathrm{mp}}=\underline{\mathscr{K}}$ has exactly the single-particle form, and it is quite clear that it commutes with terms involving only the internal coordinates and momenta. From here on we will be dealing with the Hamiltonian H in Eq. (3.40).

It is worth mentioning that much the same results would have been obtained had no specific choice of gauge been made. This is because the PZW transformation is explicitly gauge dependent [see Yang, Hirschfelder, and Johnson (1981) for details in the current notation], so that U_{PZW} would have been different than presented in Eq. (3.34). The transformed Hamiltonian would then be

$$H'=\frac{1}{2M}\left[\underline{P}-\frac{e}{c}\underline{A}(\underline{R},t)-\frac{1}{c}\underline{B}\times\underline{\mu}\right]^2+e\phi(\underline{R},t)$$
$$+T_r-\underline{\mu}\cdot\underline{E}+V\,, \tag{3.41}$$

with T_r as in Eq. (3.39) and with the total pseudomomentum having the single-particle form given in the first line of Eq. (2.9). The only explicit gauge dependence here is in the translational coordinate $\underline{R}$, and even this disappears for $e=0$.

D. Velocity boosts

It is now possible to boost the system inertially in the same manner as was done for the single particle in Sec.

II.C. The operators $\underline{\Pi}$ and $\underline{\mathscr{K}}$ obey the same commutation relations as their single-particle analogs in Eqs. (2.39). Moreover, $\underline{\mathscr{K}}$ has exactly the same form so the unitary transformation $U=\exp(-i\underline{v}\cdot\underline{G}/\hbar)$ with $\underline{G}$ as in Eq. (2.41) can be carried over *without change* to perform a velocity boost of the coordinate frame:

$$\underline{\Pi}_U=U\underline{\Pi}U^\dagger=\underline{\Pi}+M\underline{v}=\underline{P}-\frac{e}{2c}\underline{B}\times\underline{R}-\frac{1}{c}\underline{B}\times\underline{\mu}+M\underline{v}\ , \tag{3.42}$$

$$\underline{R}_U=\underline{R}+\underline{v}t\ , \tag{3.43}$$

$$\begin{aligned}\underline{\mathscr{K}}_U&=\underline{\mathscr{K}}+M\underline{v}-\frac{e}{c}\underline{v}\times\underline{B}t\\&=\underline{P}+\frac{e}{2c}\underline{B}\times\underline{R}+M(\underline{v}-\underline{v}_d)-e\left[\underline{E}+\frac{1}{c}\underline{v}\times\underline{B}\right]t\ ,\end{aligned} \tag{3.44}$$

and

$$\begin{aligned}H_U&=UHU^\dagger-i\hbar U\left[\frac{\partial}{\partial t}U^\dagger\right]\\&=\frac{1}{2M}\left[\underline{P}-\frac{e}{2c}\underline{B}\times\underline{R}-\frac{1}{c}\underline{B}\times\underline{\mu}\right]^2-e\underline{R}\cdot\left[\underline{E}+\frac{1}{c}\underline{v}\times\underline{B}\right]\\&\quad+T_r-\underline{\mu}\cdot\left[\underline{E}+\frac{1}{c}\underline{v}\times\underline{B}\right]+V\ .\end{aligned} \tag{3.45}$$

Thus the Hamiltonian transforms exactly as expected under the boost, with the fields changed according to Eqs. (1.1) and (1.2). [This was also demonstrated by Avron, Herbst, and Simon (1981) for an N-particle neutral system in a magnetic field using a completely different approach.]

Since U is of single-particle form in the multipolar gauge (it depends only upon $\underline{R}$ and $\underline{P}$), it is clear that T_r, V, and $\underline{\mu}$ (which depend only upon the internal coordinates) are unaffected by the transformation. The motional electric field dotted into $\underline{\mu}$ arises because of the coupling terms in the CM kinetic energy. Thus neglect of these coupling terms would result in the inability to add motional electric fields to $\underline{\mu}\cdot\underline{E}$.

It is also to be noted that successive boosts will result in a composite transformation of the form given in Eq. (2.45). Thus the composite transformation is generally dependent on the order of the boosts by a time-dependent multiplier unless the system is electrically neutral ($e=0$), or unless $B=0$.

By choosing $\underline{v}$ to be the drift velocity, H_U of Eq. (3.45) reduces to

$$H_U=\frac{\Pi^2}{2M}-eE_{||}Z+T_r-E_{||}\mu_z+V\ . \tag{3.46}$$

It is clear that $\mathscr{K}_x^0$ and $\mathscr{K}_y^0$ commute with H_U. For charged systems, diagonalization of either of them, or of $(\mathscr{K}_x^0)^2+(\mathscr{K}_y^0)^2$, may be accomplished as in the case of a single charged particle. For neutral systems, $\mathscr{K}_x^0=P_x$ and $\mathscr{K}_y^0=P_y$, so both may be simultaneously diagonalized. (The coordinate Z is separable in either case.)

This Hamiltonian has yet another constant of the motion, the total canonical angular momentum component L_{tz} in Eq. (3.17). Using Eq. (3.30), we can express this as

$$L_{tz}=\sum_{i=1}^{N}(X_iP_{iy}-Y_iP_{ix})\ . \tag{3.47}$$

The same trick used in Sec. II.E for the single particle may also be employed here. We may boost L_{tz} back to the lab frame, inverting the *PZW* transformation as well, to find

$$\begin{aligned}U_{\rm PZW}^\dagger U^\dagger\sum_{i=1}^{N}[\underline{R}_i\times\underline{P}_i]_z UU_{\rm PZW}&=\sum_{i=1}^{N-1}\left[\underline{R}_i\times\left[\underline{P}_i-\frac{\varepsilon_{iN}}{2c}\underline{B}\times\underline{R}\right]\right]_z+\left[(\underline{R}-\underline{v}_dt)\times\left[\underline{P}-M\underline{v}_d+\frac{1}{2c}\underline{B}\times\underline{\mu}-\frac{e\underline{E}t}{2}\right]\right]_z\\&=\sum_{i=1}^{N}\left[(\underline{r}_i-\underline{v}_dt)\times\left[\underline{P}_i-m_i\underline{v}_d\frac{e_i\underline{E}t}{2}\right]\right]_z\ .\end{aligned} \tag{3.48}$$

This is an explicitly time-dependent constant of the motion for N particles in constant $\underline{E}$ and $\underline{B}$. Comparison with Eq. (2.95) shows it to be the sum of the single-particle analogs.

Throughout this paper we have considered only the nonrelativistic formulation. For a theory capable of being compared with very precise experimental measurements, semirelativistic corrections (of order α^2 relative to nonrelativistic terms, where α is the fine-structure constant) can also be necessary. These corrections have been theoretically examined to some extent for low-lying states of hydrogenic systems in both weak and strong magnetic fields (Grotch and Hegstrom, 1971; Angelié and Deutsch, 1978; Virtamo and Lindgren, 1979; Lindgren and Virtamo, 1979; Doman, 1980). It seems to us that a useful, if ambitious, project would be to extend the current nonrelativistic results to a single-time positive-energy Hamiltonian such as the Breit-Pauli Hamiltonian $H_{\rm BP}$ (Bethe and Salpeter, 1957) including constant external fields. For example, can one demonstrate that $H_{\rm BP}(\underline{E},\underline{B})$ becomes, under an inertial boost of velocity $\underline{v}$, simply $H_{\rm BP}(\underline{E}',\underline{B}')$, where $\underline{E}'$ and $\underline{B}'$ are the Lorentz-transformed fields? [Here it is implied that these Hamiltonians differ only in the values of $\underline{E}$ and $\underline{B}$ inserted, just as for the nonrelativistic example in Eq. (2.37). Of course, to be consistent, terms of higher order in $\underline{v}/c$ than were kept in Eqs. (1.1) and (1.2) would have to be retained in the Lorentz transformation of the fields. See Landau and Lifshitz (1975), Jackson (1975).] Note that the spin and orbital motions are coupled in $H_{\rm BP}$ and must be treated simul-

taneously; a complication avoided nonrelativistically. We believe that treatment of the CM (velocity boost, CM separation, or coupling to the internal degrees of freedom) for such Hamiltonians can be greatly simplified by combining the ideas of the PZW transformation with the research of Krajcik and Foldy (Krajcik and Foldy, 1970, 1974; Foldy and Krajcik, 1974, 1975; Sebastian and Yun, 1979; Yang, Hirschfelder, and Johnson, 1981), who have shown how the CM can be separated semirelativistically if there are no external fields.

E. Velocity boosts along a single-particle classical path

For a single charged particle in combined $\underline{E}$ and $\underline{B}$, wave packets centered around a classical path were generated in Sec. II.F. It is not possible simply to generalize that treatment to molecular wave packets which localize the CM about a prescribed trajectory, since the coupling between the CM and internal coordinates must be taken into account. At best we expect that approximate methods could be developed for which the zeroth-order approximation would have the CM following a single-particle path $\underline{R}_{\rm cl}$ (see Appendix A).

Under the unitary transformation $\mathscr{U}$ of Eqs. (2.96), (2.97), and (2.100), the single-particle Hamiltonian was transformed into the time-independent form for a particle in a magnetic field, allowing wave packets in the lab frame to be generated from stationary states in the accelerated frame. Applying this transformation to the N-particle multipolar Hamiltonian H in Eq. (3.40), we obtain

$$H_{\mathscr{U}}=\frac{\Pi^2}{2M}+T_r+V-\underline{\mu}\cdot\left[\underline{E}+\frac{1}{c}\dot{\underline{R}}_{\rm cl}\times\underline{B}\right]. \tag{3.49}$$

Just as for the single particle, the term $-e\underline{E}\cdot\underline{R}$ has disappeared under the boost to the new frame, and all factors involving the CM degrees of freedom are explicitly time independent. However, the electric field "experienced" by the internal coordinates now has a motional contribution involving $\dot{\underline{R}}_{\rm cl}$, which varies harmonically with the cyclotron frequency. The new Hamiltonian thus has explicit time dependence, although of very low frequency. We have introduced a classical trajectory for the low-frequency motion, similar in spririt to the adiabatic approximation for nuclear motion, but with no approximations made so far. These come into solving for the (nonstationary) wave functions for $H_{\mathscr{U}}$ which, when boosted back to the lab frame, become packets.

We note that, if the system is neutral, then $\underline{R}_{\rm cl}=\underline{R}_0+\underline{v}t$, and $H_{\mathscr{U}}$ is time independent. In fact, the inertial boost U of Eqs. (2.34) and (2.41) coincides with $\mathscr{U}$ of Eqs. (2.96) and (2.97) for this case. Thus $H_{\mathscr{U}}$ is identical to H_U of Eq. (3.45) for $e=0$.

It is a little out of the ordinary to deal with time-dependent wave functions for static fields. In a related context, though, we mention the possibility of nonrelativistic extensions to time- and position-dependent electromagnetic fields in a long-wavelength approximation. If the vector and scalar potentials for a single particle are expanded about some position, and we retain only terms which make the resulting single-particle Hamiltonian quadratic in the coordinate and momenta, time-dependent linear constants of the motion (Malkin and Man'ko, 1968, 1970; Malkin, Man'ko, and Trifonov, 1970, 1973) and wave functions can fairly easily be obtained. However, we have not seen any analogous investigations of CM motion or separation for molecular systems, where the long-wavelength approximation would correspond to inclusion of electric dipole, magnetic dipole, and electric quadrupole interactions.

IV. WAVE FUNCTIONS FOR NEUTRAL SYSTEMS IN CONSTANT $\underline{E}$ AND $\underline{B}$

In the last section, atomic and molecular systems were considered without specifying the net charge. Here we examine the simpler case of *neutral systems* (neglecting spin, as mentioned in Sec. III.A). This was explored in depth for N particles in a magnetic field by Avron, Herbst, and Simon (1978). The inclusion of an electric field is not difficult in any event, and is especially trivial for neutral systems (Carter, 1967; Gor'kov and Dzyaloshinskii, 1967). The reason is that, in the multipolar gauge, the total pseudomomentum $\underline{\mathscr{K}}$ reduces to the canonical momentum $\underline{P}$ apart from a constant term. Since all components therefore commute, they may be simultaneously diagonalized and the Schrödinger equation reduced to an effective one for the internal coordinates.

It is in the latter equation that the "motional electric field" experienced by the internal degrees of freedom arises (Lamb, 1952). This motional field is *not,* however, directly connected to the velocity of the CM, as is often assumed. Actually, such an assumption is not bad for magnetic fields attainable in the laboratory, but proof of this is certainly more involved than might be expected at first glance. This point is examined later for two oppositely charged particles in a magnetic field, both for a model problem with harmonic interaction and for the ground and first excited states of the hydrogen atom.

A. Pseudoseparation of the CM

For $e=0$, Eqs. (3.37), (3.38), and (3.40) give us, in the multipolar gauge,

$$H=\frac{\Pi^2}{2M}+T_r+V-\underline{\mu}\cdot\underline{E}\,, \tag{4.1}$$

$$\underline{\Pi}=\underline{P}-\frac{1}{c}\underline{B}\times\underline{\mu}\,, \tag{4.2}$$

$$\underline{\mathscr{K}}=\underline{P}-M\underline{v}_d\,. \tag{4.3}$$

All components of $\underline{\Pi}$ and of $\underline{\mathscr{K}}$ commute for this case, and $\underline{\mathscr{K}}$ could be given the vector eigenvalue $\hbar\underline{K}$. For neutral systems, it is more convenient for our purposes to assign this eigenvalue to

$$\underline{\mathscr{K}}^0=\underline{P}\ , \tag{4.4}$$

which clearly amounts merely to the redefinition $\hbar\underline{K}\rightarrow\hbar\underline{K}-M\underline{v}_d$. The new convention for the meaning of $\underline{K}$ is therefore frame dependent [it coincides with the old one only when we are working in the drift frame ($E_\perp=0$)], and is adopted *in this section only.*

Thus the full time-independent wave function $\psi(\underline{R}_1\cdots\underline{R}_{N-1},\underline{R})$ satisfies

$$[H-\mathscr{E}]\psi=0\ , \tag{4.5}$$

$$[\underline{P}-\hbar\underline{K}]\psi=0\ . \tag{4.6}$$

Equation (4.6) is obviously solved by

$$\psi(\underline{R}_1\cdots\underline{R}_{N-1},\underline{R})=\exp(i\underline{K}\cdot\underline{R})\chi(\underline{R}_1\cdots\underline{R}_{N-1})\ . \tag{4.7}$$

Inserting Eqs. (4.1) and (4.7) into Eq. (4.5), we replace $\underline{P}$ with $\hbar\underline{K}$, yielding the effective equation obeyed by the internal wave function χ,

$$\left[\frac{1}{2M}\left[\hbar\underline{K}-\frac{1}{c}\underline{B}\times\underline{\mu}\right]^2+T_r+V-\underline{\mu}\cdot\underline{E}-\mathscr{E}\right]\chi=0\ . \tag{4.8}$$

Upon expanding the quantity representing the CM kinetic energy,

$$\frac{1}{2M}\left[\hbar\underline{K}-\frac{1}{c}\underline{B}\times\underline{\mu}\right]^2=\frac{\hbar^2K^2}{2M}-\frac{\hbar}{Mc}\underline{K}\times\underline{B}\cdot\underline{\mu}+\frac{1}{2Mc^2}(\underline{B}\times\underline{\mu})^2\ , \tag{4.9}$$

three terms result having the appearances of a kinetic energy, a motional Stark term, and a contribution to the internal diamagnetic terms, respectively. Equation (4.8) can be recast as an equation for an internal Hamiltonian depending on $\underline{K}_\perp$, the component of $\underline{K}$ perpendicular to $\underline{B}$,

$$(h-\mathscr{E}_{\rm int})\chi=0\ , \tag{4.10}$$

where

$$h=T_r+V-\underline{\mu}\cdot\left[\underline{E}+\frac{\hbar}{Mc}\underline{K}_\perp\times\underline{B}\right]+\frac{1}{2Mc^2}(\underline{B}\times\underline{\mu})^2\ , \tag{4.11}$$

$$\mathscr{E}_{\rm int}=\mathscr{E}-\frac{\hbar^2K^2}{2M}\ . \tag{4.12}$$

Thus the effective electric field seen by the internal degrees of freedom is $\underline{E}+(\hbar/Mc)\underline{K}_\perp\times\underline{B}$, which is of the form $\underline{E}'=\underline{E}+(1/c)\underline{v}\times\underline{B}$ given in Eq. (1.1). It is to be noted that the internal Hamiltonian h and the internal energy $\mathscr{E}_{\rm int}$ are invariant under a boost of the system to a moving frame, since then $\underline{K}_\perp$ and $\underline{E}_\perp$ will undergo changes which compensate each other in the sum $\underline{E}_\perp+(\hbar/Mc)\underline{K}_\perp\times\underline{B}$.

For completeness, the wave function in the representation in which the individual particles are minimally coupled to the external fields is obtained by applying the inverse of the PZW transformation in Eq. (3.34),

$$\psi_{\rm mc}=U^\dagger_{\rm PZW}\psi=\exp[i(\underline{K}+\underline{\mu}\times\underline{B}/2\hbar c)\cdot\underline{R}\,]\chi(\underline{R}_1\cdots\underline{R}_{N-1})\ . \tag{4.13}$$

It should be clear that calculations are somewhat easier in the multipolar gauge, where $\psi\equiv\psi_{\rm mp}$ is given by Eq. (4.7). For instance, the neutral velocity boost generator is then simply $\underline{G}_0=M\underline{R}-\underline{P}t$ of Eq. (2.26), whereas it will involve the dipole moment in the minimal coupling representation.

The reduction of Eq. (4.5) to (4.10) is called *pseudoseparation* of the CM, since h depends upon the eigenvalue $\hbar K_\perp$. In other respects, it closely resembles the ordinary separation in the absence of external fields.[8] One important difference, which Avron, Herbst, and Simon (1978, 1981) and Herold, Ruder, and Wunner (1981) explicitly note, since it is occasionally overlooked, is that $\hbar\underline{K}_\perp/M$ does *not* represent the transverse velocity of the CM except in the limit that the magnetic field vanishes. Comparing the components of Eqs. (4.2) and (4.4) in the plane perpendicular to $\underline{B}$, we have

$$\underline{\Pi}_\perp=\underline{K}^0_\perp-\frac{1}{c}\underline{B}\times\underline{\mu}\ , \tag{4.14}$$

so that the transverse CM velocity has an additional term involving the dipole moment. It is anticipated that, on the average, the contribution of the last term in Eq. (4.14) will be small. Taking the expectation value with ψ of Eq. (4.7) and integrating only over the internal coordinates, we obtain

$$\langle\psi\,|\,\underline{\Pi}_\perp\,|\,\psi\rangle=\hbar\underline{K}_\perp-\frac{1}{c}\langle\chi\,|\,\underline{B}\times\underline{\mu}\,|\,\chi\rangle\ . \tag{4.15}$$

(In the direction of $\underline{B}$, we have simply $\langle\Pi_z\rangle=\langle P_z\rangle=\hbar K_z$ for $E_{||}=0$.) The last term should be relatively unimportant for either weak magnetic fields or weak polarization of the internal wave function. For

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[8] In connection with Sec. III.E, we note that a molecular wave packet for a neutral system can be formally constructed in analogy to the procedure for a free particle (see Darwin, 1928):

$$\Psi(\underline{R}_1\cdots\underline{R}_{N-1},\underline{R},t)=\int d\underline{K}\,\phi(\underline{K})\exp(-i\mathscr{E}t/\hbar)\psi(\underline{R}_1\cdots\underline{R}_{N-1},\underline{R})$$
$$=\int d\underline{K}\,\phi(\underline{K})\exp\left[-\frac{it}{\hbar}\left[\mathscr{E}_{\rm int}+\frac{\hbar^2K^2}{2M}\right]+i\underline{K}\cdot\underline{R}\right]\times\chi(\underline{R}_1\cdots\underline{R}_{N-1})\ .$$

Here the amplitude function $\phi(\underline{K})$ produces a wave function which localizes the CM, and $\mathscr{E}_{\rm int}$ and χ depend upon $\underline{K}_\perp$, as in Eq. (4.10). Although the quantities in the integrand are not known exactly, Ψ might be evaulated approximately, say, by using the free-particle form of $\phi(\underline{K})$ and a perturbation expansion of the internal wave function and energy.

atomic or other systems with no permanent dipole moment, it can be smaller (of higher order in B) than for polyatomic nonlinear molecules with permanent dipole moments.

The fact that $\langle \underline{\Pi}_\perp \rangle$ is not the same thing as $\hbar \underline{K}_\perp$ (which is what enters into the motional electric field relevant to the internal degrees of freedom) is demonstrated classically in Sec. IV.B for an exactly solvable model problem. After that, perturbative estimates of the last term in Eq. (4.15) are made for atomic hydrogen in a magnetic field, showing quantitatively that the differences between $\langle \underline{\Pi}_\perp \rangle$ and $\hbar \underline{K}_\perp$ are very small for the ground and first excited states. However, this difference should be much larger for highly excited states.

B. Neutral two-body system assuming harmonic interaction

Avron, Herbst, and Simon (1978) have shown that the problem of a neutral two-body system with *equal masses, harmonic interaction,* and an external magnetic field can be solved exactly. Herold, Ruder, and Wunner (1981) have further worked out the quantum-mechanical details for unequal masses. We present solutions to the *classical equations of motion for general masses* in order to discuss the role played by the total pseudomomentum. (One could also add an external electric field; this is again the same as a redefinition of $\underline{K}_\perp$ as far as the perpendicular field is concerned.) It should be clear that the pseudomomentum is equally applicable to classical pseudoseparation of the CM.

The particles are taken to have charges $e_1=-q$ and $e_2=q$, with $q>0$. The dipole moment is hereafter eliminated in favor of the interparticle distance $\underline{\rho}$,

$$\underline{\mu}=-q\underline{\rho}=-q(\underline{r}_1-\underline{r}_2)\ . \tag{4.16}$$

The (scalar) symbol μ now stands for the reduced mass

$$\mu=\frac{m_1 m_2}{M}\ . \tag{4.17}$$

The potential V is simply

$$V=\tfrac{1}{2}\mu\omega_0^2\rho^2\ . \tag{4.18}$$

The motion of the internal coordinate z is completely separable and just that of an ordinary one-dimensional harmonic oscillator of frequency ω_0. Since this holds no interest for us, we confine our attention to the motion perpendicular to $\underline{B}$. From the details of Appendix B, the transverse Hamiltonian is obtained as

$$H_\perp=\frac{1}{2M}\left[\underline{P}_\perp+\frac{q}{c}\underline{B}\times\underline{\rho}_\perp\right]^2 + \frac{1}{2\mu}\left[\underline{\pi}_\perp+\frac{q}{2c}\frac{m_2-m_1}{M}\underline{B}\times\underline{\rho}_\perp\right]^2+\frac{\mu}{2}\omega_0^2\rho_\perp^2\ , \tag{4.19}$$

with $\underline{\pi}_\perp$ the canonical momentum conjugate to $\underline{\rho}_\perp$.

The total two-dimensional pseudomomentum (which is also the total canonical momentum for this case) is

$$\underline{P}_\perp=\hbar\underline{K}_\perp=M\dot{\underline{R}}_\perp-\frac{q}{c}\underline{B}\times\underline{\rho}_\perp\ , \tag{4.20}$$

where $\hbar\underline{K}_\perp$ is a given constant chosen in analogy with the quantum-mechanical problem. From Eqs. (4.19) and (4.20), the equations of motion for x and y, are

$$\begin{aligned}\dot{x}&=\frac{1}{\mu}\pi_x-\eta y\ ,\\ \dot{y}&=\frac{1}{\mu}\pi_y+\eta x\ ,\end{aligned} \tag{4.21}$$

and

$$\begin{aligned}\ddot{x}&=-2\eta\dot{y}-\frac{qB}{\mu Mc}\hbar K_y-\omega_1^2 x\ ,\\ \ddot{y}&=2\eta\dot{x}+\frac{qB}{\mu Mc}\hbar K_x-\omega_1^2 y\ ,\end{aligned} \tag{4.22}$$

with

$$\eta=\frac{qB}{2c}\frac{m_2-m_1}{\mu M}=\frac{qB}{2c}\left[\frac{1}{m_1}-\frac{1}{m_2}\right] \tag{4.23}$$

and

$$\omega_1^2=\omega_0^2+\frac{q^2B^2}{\mu Mc^2}=\omega_0^2-\omega_1\omega_2\ , \tag{4.24}$$

$$\omega_1=-\frac{qB}{m_1 c}\ , \tag{4.25}$$

$$\omega_2=\frac{qB}{m_2 c}\ . \tag{4.26}$$

(The individual cyclotron frequencies here are negative or positive, depending on the sign of the charge, as in Sec. II.)

Equations (4.22) are solved by elementary means. The results are

$$\underline{\rho}_\perp=\underline{Q}_--\underline{Q}_+-\frac{q\hbar}{\mu M\omega_1^2 c}\underline{K}_\perp\times\underline{B}\ , \tag{4.27}$$

where $\underline{Q}_\pm$ are two-dimensional normal coordinates for separate circular motions

$$\underline{Q}_\pm=\rho_\pm[\hat{\underline{x}}\sin(\omega_\pm t+\phi_\pm)+\hat{\underline{y}}\cos(\omega_\pm t+\phi_\pm)]\ , \tag{4.28}$$

$$\omega_\pm=\pm\xi-\eta\ , \tag{4.29}$$

$$\xi=(\omega_1^2+\eta^2)^{1/2}=\left[\omega_0^2+\frac{q^2B^2}{4\mu^2c^2}\right]^{1/2}\ . \tag{4.30}$$

Since $\omega_\pm\gtrless 0$, the two motions are rotating in opposite senses. Equation (4.27) may be substituted into Eq. (4.20), which is then integrated to obtain

$$\underline{R}_\perp=\underline{C}_\perp+\frac{1}{M}\hbar\underline{K}_\perp\frac{\omega_0^2}{\omega_1^2}t+\frac{qB}{Mc}\left[\frac{1}{\omega_+}\underline{Q}_+-\frac{1}{\omega_-}\underline{Q}_-\right]\ , \tag{4.31}$$

where $\underline{C}_\perp$ is a constant vector. The results of Eqs. (4.27) and (4.31), when inserted into Eq. (4.19), yield the energy

$$\mathscr{E}_\perp=\frac{\hbar^2K_\perp^2}{2M}\frac{\omega_0^2}{\omega_\perp^2}+\mu\xi(\rho_-^2|\omega_-|+\rho_+^2|\omega_+|)\,. \tag{4.32}$$

Thus $\underline{R}_\perp$ and $\underline{\rho}_\perp$ both contain components describing bounded oscillatory motion, but, for $\underline{R}_\perp$, these are superimposed upon a uniform translational motion. This agrees with the quantum-mechanical result of Herold, Ruder, and Wunner (1981)

$$\langle\underline{\Pi}_\perp\rangle=\hbar\underline{K}_\perp\frac{\omega_0^2}{\omega_\perp^2}=\hbar\underline{K}_\perp\left[1+\frac{q^2B^2}{m_1m_2c^2\omega_0^2}\right]^{-1}, \tag{4.33}$$

namely, that the average transverse mechanical momentum is proportional to $\hbar\underline{K}_\perp$, but with a constant of proportionality (≤ 1) that depends upon the interaction.

As $B\to 0$, we have from Eqs. (4.23), (4.24), (4.29), and (4.30) that

$$\begin{aligned}&\eta\to 0\,,\\&\xi\to\omega_0\,,\\&\omega_\perp\to\omega_0\,,\\&\omega_\pm\to\pm\omega_0\,,\end{aligned} \tag{4.34}$$

and so

$$\underline{Q}_\pm=\rho_\pm[\hat{\underline{x}}\sin(\pm\omega_0t+\phi_\pm)+\hat{\underline{y}}\cos(\pm\omega_0t+\phi_\pm)]\,. \tag{4.35}$$

With some reparametrization, Eq. (4.27) becomes

$$\underline{\rho}_\perp=\hat{\underline{x}}\left[x_0\cos\omega_0t+\frac{\dot{x}_0}{\omega_0}\sin\omega_0t\right]+\hat{\underline{y}}\left[y_0\cos\omega_0t+\frac{\dot{y}_0}{\omega_0}\sin\omega_0t\right], \tag{4.36}$$

and Eq. (4.31) reduces to

$$\underline{R}_\perp=\underline{C}_\perp+\frac{1}{M}\hbar\underline{K}_\perp t\,. \tag{4.37}$$

For $B=0$, the internal motion is that of a simple harmonic oscillator, and $\underline{R}_\perp$ follows a free-particle trajectory with initial position $\underline{C}_\perp$ and with $\hbar\underline{K}_\perp/M$ representing the constant velocity. The energy $\mathscr{E}_\perp$ of Eq. (4.32) then includes the CM kinetic energy $\hbar^2K_\perp^2/2M$.

In the limit that $\omega_0\to 0$, however, we obtain

$$\begin{aligned}&\omega_\perp^2\to\omega_1\omega_2=\frac{q^2B^2}{m_1m_2c^2}\\&\omega_-\to\omega_1=-\frac{qB}{m_1c}\\&\omega_+\to\omega_2=\frac{qB}{m_2c}\,,\end{aligned} \tag{4.38}$$

and the normal coordinates become those for noninteracting particles in a magnetic field

$$\begin{aligned}&\underline{Q}_-\to\underline{Q}_1=\rho_-[\hat{\underline{x}}\sin(\omega_1t+\phi_-)+\hat{\underline{y}}\cos(\omega_1t+\phi_-)]\,,\\&\underline{Q}_+\to\underline{Q}_2=\rho_+[\hat{\underline{x}}\sin(\omega_2t+\phi_+)+\hat{\underline{y}}\cos(\omega_2t+\phi_+)]\,.\end{aligned} \tag{4.39}$$

The constant term in Eq. (4.27) becomes, according to Eq. (3.16),

$$\frac{q\hbar}{\mu M\omega_\perp^2c}\underline{B}\times\underline{K}_\perp\to\frac{c}{qB^2}\underline{B}\times\left[-\frac{q}{c}\underline{B}\times\underline{r}_{1c}+\frac{q}{c}\underline{B}\times\underline{r}_{2c}\right]=\underline{r}_{1c}-\underline{r}_{2c}\,, \tag{4.40}$$

where $\underline{r}_{1c}$ and $\underline{r}_{2c}$ are the vectors locating the centers of the individual orbits. [See discussion of Eq. (3.16).] Thus Eq. (4.27) becomes

$$\underline{\rho}_\perp=\underline{r}_{1\perp}-\underline{r}_{2\perp}=\underline{Q}_1+\underline{r}_{1c}-\underline{Q}_2-\underline{r}_{2c}\,, \tag{4.41}$$

while Eq. (4.31) is, in this case,

$$\underline{R}_\perp=\underline{C}_\perp+\frac{m_1}{M}\underline{Q}_1+\frac{m_2}{M}\underline{Q}_2\,. \tag{4.42}$$

The constant $\underline{C}_\perp$ is now identified as $(m_1\underline{r}_{1c}+m_2\underline{r}_{2c})/M$. Both particles execute circular motion, and the CM has no net transverse velocity. The constant $\hbar\underline{K}_\perp/M$ is associated with the charge centroid of guiding centers of the orbits instead of an average CM velocity. The energy $\mathscr{E}_\perp$ is now independent of $K_\perp$. For the details of the quantum-mechanical treatment, see Herold, Ruder, and Wunner (1981).

While the above is only a special case, it does illustrate quite clearly that the separation constant $\hbar\underline{K}_\perp/M$, which enters into the effective electric field for the internal degrees of freedom, is not identical to the average transverse velocity of the system. The expectation is, as mentioned earlier, that this discrepancy is small for most molecular applications in the laboratory. We now proceed to the neutral two-body system with Coulomb interaction.

C. Perturbed wave functions for a two-body Coulomb system in a magnetic field

Since the problem of a hydrogenic system in a magnetic field cannot be solved in closed form, we resort to perturbation theory. In the following, wave functions through first order in the magnetic field strength are evaluated for principal quantum numbers $n=1$ and $n=2$, which will then allow us to obtain the expectation value on the right side of Eq. (4.15) through second order. Atomic units are used,

$$\mu=\hbar=a_0=1\,, \tag{4.43}$$

and the unit of length, $a_0=\hbar^2/\mu q^2$, is the first Bohr radius based on the reduced mass. It is also convenient to use, in place of $\underline{B}$, the dimensionless magnetic field

$$\underline{\gamma}=\underline{B}/B_0\,, \tag{4.44}$$

with $B_0=\hbar c/qa_0^2$ ($=2.35\times10^9$ G for atomic hydrogen).

The magnitude γ is dimensionless.

The internal Hamiltonian h of Eq. (4.11) with $E=0$ and $N=2$ is then reduced to (see Appendix B)

$$h=-\tfrac{1}{2}\nabla^2-\frac{1}{\kappa}+\frac{1}{M}\underline{K}_\perp\times\underline{\gamma}\cdot\underline{\kappa}-i\beta\underline{\gamma}\cdot\underline{\kappa}\times\nabla+\tfrac{1}{8}(\underline{\gamma}\times\underline{\kappa})^2 , \tag{4.45}$$

where

$$\beta=\frac{m_2-m_1}{2M} , \tag{4.46}$$

which goes to $\frac{1}{2}$ as $m_1/m_2\to 0$.

We now want to perturbatively solve Eq. (4.10), which is written as

$$(h-\mathscr{E})\chi(\kappa)=0 . \tag{4.47}$$

Accordingly, h, χ, and $\mathscr{E}$ are expanded in powers of γ. Taking $\underline{K}_\perp$ to be in the x direction, we have

$$h=h^{(0)}+\gamma h^{(1)}+\gamma^2 h^{(2)} , \tag{4.48}$$

where

$$h^{(0)}=-\tfrac{1}{2}\nabla^2-\frac{1}{\kappa} , \tag{4.49}$$

$$h^{(1)}=-\frac{K_\perp}{M}y-i\beta\left[x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right] , \tag{4.50}$$

$$h^{(2)}=\tfrac{1}{8}(x^2+y^2) , \tag{4.51}$$

and

$$\chi=\sum_{i=0}^{\infty}\gamma^i\chi^{(i)} , \tag{4.52}$$

$$\mathscr{E}=\sum_{i=0}^{\infty}\gamma^i\mathscr{E}^{(i)} . \tag{4.53}$$

Since the wave functions are to be determined only through first order, the relevant equations arising from expansion of Eq. (4.47) are those of zeroth and first order in γ,

$$\bar{h}^{(0)}\chi^{(0)}=0 , \tag{4.54}$$

$$\bar{h}^{(0)}\chi^{(1)}+\bar{h}^{(1)}\chi^{(0)}=0 , \tag{4.55}$$

where

$$\bar{h}^{(i)}=h^{(i)}-\mathscr{E}^{(i)} . \tag{4.56}$$

The unperturbed energy is, of course,

$$\mathscr{E}^{(0)}=-\frac{1}{2n^2} , \tag{4.57}$$

and (for $\langle\chi^{(0)}\,|\,\chi^{(0)}\rangle=1$) the first-order energy is obtained from

$$\mathscr{E}^{(1)}=\langle\chi^{(0)}\,|\,h^{(1)}\,|\,\chi^{(0)}\rangle . \tag{4.58}$$

There are several ways of solving the first-order equation for $\chi^{(1)}$ once $\mathscr{E}^{(1)}$ has been determined. We have chosen one which is equivalent (for the ground state) to the F-operator method of Dalgarno and Lewis (1955).[9] From numerous examples of hydrogenic perturbation theory [particularly that of Lambin, Van Hay, and Kartheuser (1978), which is closely related to our problem], $\chi^{(i)}$ is known to have the form

$$\chi^{(i)}(\underline{\kappa})=F^{(i)}(\underline{\kappa})e^{-\kappa/n} , \tag{4.59}$$

where $F^{(i)}$ is a finite polynomial in the coordinates. Thus, defining

$$\bar{\eta}_n^{(0)}=e^{\kappa/n}\bar{h}^{(0)}e^{-\kappa/n}=-\tfrac{1}{2}\nabla^2+\frac{1}{n}\hat{\kappa}\cdot\nabla+\frac{1-n}{n\kappa} , \tag{4.60}$$

$F^{(1)}$ must satisfy

$$\bar{\eta}_n^{(0)}F^{(1)}=-\bar{h}^{(1)}F^{(0)} . \tag{4.61}$$

[Only $\bar{h}^{(0)}$ is affected by the Eq. (4.60) similarity transformation with $\exp(\kappa/n)$.] Given a specific $F^{(0)}$, the exact form of the right side is known, and it is only a matter of algebra to find a particular solution $F^{(1)}$.

As presented, Eq. (4.61) assumes that $\chi^{(0)}$ is nondegenerate, and is thus applicable to the ground state $n=1$. We shall not go through the details here, but do give the useful recursion relation

$$\bar{\eta}_1^{(0)}\kappa^j x^k y^l=(j+k+l)\kappa^{j-1}x^k y^l-\frac{j(j+1+2k+2l)}{2}\kappa^{j-2}x^k y^l-\frac{k(k-1)}{2}\kappa^j x^{k-2}y^l-\frac{l(l-1)}{2}\kappa^j x^k y^{l-2} . \tag{4.62}$$

This facilitates systematic solution of Eq. (4.61), or especially of the analogous higher-order equations encountered when the calculation is pursued beyond first order. Through first order, for $\chi^{(1)}$ orthogonal to $\chi^{(0)}$, we have

$$\chi^{(0)}=\pi^{-1/2}e^{-\kappa} , \tag{4.63}$$

$$\mathscr{E}^{(0)}=-\tfrac{1}{2} , \tag{4.64}$$

$$\chi^{(1)}=\pi^{-1/2}\frac{K_\perp}{M}\left[1+\frac{\kappa}{2}\right]ye^{-\kappa} , \tag{4.65}$$

$$\mathscr{E}^{(1)}=0 . \tag{4.66}$$

For $n=2$, there is a further complication due to the extra degeneracy of the excited states. The correct zeroth-order basis functions must be obtained which diagonalize $h^{(1)}$ of Eq. (4.50). Otherwise, the analog of the first-order equations (4.55) or (4.61) is a set of equations coupled between the different states. For $K_\perp=0$, i.e., no electric field term, the correct basis is the set of spherical coordi-

[9] A. Maquet has brought to our attention that elements of the F-operator technique were used earlier for the Dirac equation by Brown, Peierls, and Woodward (1954) and by Brenner, Brown, and Woodward (1954).

nate functions Φ_{2lm},

$$\begin{aligned}
\Phi_{200}&=\tfrac{1}{4}(2\pi)^{-1/2}(2-\rho)e^{-\rho/2}\,,\\
\Phi_{21-1}&=\tfrac{1}{8}\pi^{-1/2}(x-iy)e^{-\rho/2}\,,\\
\Phi_{210}&=\tfrac{1}{4}(2\pi)^{-1/2}ze^{-\rho/2}\,,\\
\Phi_{211}&=-\tfrac{1}{8}\pi^{-1/2}(x+iy)e^{-\rho/2}\,.
\end{aligned}\tag{4.67}$$

On the other hand, for an electric field alone, the Schrödinger equation will separate in parabolic coordinates, and the appropriate basis is then a set of parabolic functions. However, neither of these choices will generally diagonalize $h^{(1)}$.

The solution to this problem was given in an elegant paper by Demkov, Monozon, and Ostrovskii (1969). They showed that the $O(4)$ symmetry of the hydrogen atom allows diagonalization of the sum of Stark and linear Zeeman terms within any multiplet of constant n. Adapting their results to the case at hand, we find an appropriate orthonormal basis to be

$$\begin{aligned}
\chi_a^{(0)}&=\tfrac{1}{8}\pi^{-1/2}[ig(2-\rho)+fx-iy]e^{-\rho/2}\,,\\
\chi_b^{(0)}&=\tfrac{1}{4}(2\pi)^{-1/2}[f(2-\rho)+igx]e^{-\rho/2}\,,\\
\chi_c^{(0)}&=-\tfrac{1}{8}\pi^{-1/2}[ig(2-\rho)+fx+iy]e^{-\rho/2}\,,\\
\chi_d^{(0)}&=\tfrac{1}{4}(2\pi)^{-1/2}ze^{-\rho/2}\,,
\end{aligned}\tag{4.68}$$

where

$$f=\beta/\nu\,,\tag{4.69}$$

$$g=3K_\perp/M\nu\,,\tag{4.70}$$

$$\nu=[(3K_\perp/M)^2+\beta^2]^{1/2}\,.\tag{4.71}$$

These functions may easily be shown to be related by a unitary transformation to the spherical functions Φ_{2lm} in Eqs. (4.67). In fact, they reduce to the latter in the limit $K_\perp\to 0$, that is, $f\to 1$ and $g\to 0$.

The first-order energy matrix is now diagonal with eigenvalues

$$\begin{aligned}
\mathscr{E}_a^{(1)}&=-\nu\,,\\
\mathscr{E}_b^{(1)}&=0\,,\\
\mathscr{E}_c^{(1)}&=+\nu\,,\\
\mathscr{E}_d^{(1)}&=0\,.
\end{aligned}\tag{4.72}$$

From the form of ν in Eq. (4.71), two familiar limits are seen to be contained in Eqs. (4.72). For $3K_\perp/M\gg\beta$, one obtains the linear Stark energies for the $n=2$ multiplet. For $3K_\perp/M\ll\beta$, on the other hand, the linear Zeeman energies (with finite nuclear mass effects taken into account) are obtained. With the first-order energy diagonal, it is now possible to calculate each $\chi^{(1)}$ independently. We mention, however, that the calculations for a, b, and c become coupled starting in second order, and require the methods of almost degenerate perturbation theory (e.g., Hirschfelder, 1978; see Sec. V.D) if pursued further than we have here. State d is always uncoupled from the other three, since it is the only one that is odd under inversion of z, a characteristic which persists through all orders.

For each state, $F^{(0)}$ is readily extracted from Eqs. (4.68) and $\bar{h}^{(1)}$ found from Eqs. (4.50), (4.56), and (4.72), providing the specific form of the right side of Eq. (4.61). Solution of the latter equation is then easily accomplished by use of the two recursion relations

$$\bar{\eta}_2^{(0)}\rho^j x^k y^l=\frac{j+k+l-1}{2}\rho^{j-1}x^k y^l-\frac{j(j+1+2k+2l)}{2}\rho^{j-2}x^k y^l-\frac{k(k-1)}{2}\rho^j x^{k-2}y^l-\frac{l(l-1)}{2}\rho^j x^k y^{l-2}\tag{4.73}$$

and

$$\bar{\eta}_2^{(0)}\rho^j x^k y^l z=\frac{j+k+l}{2}\rho^{j-1}x^k y^l z-\frac{j(j+3+2k+2l)}{2}\rho^{j-2}x^k y^l z-\frac{k(k-1)}{2}\rho^j x^{k-2}y^l z-\frac{l(l-1)}{2}\rho^j x^k y^{l-2}z\,.\tag{4.74}$$

Passing directly to the results, we obtain

$$\begin{aligned}
\chi_a^{(1)}&=\frac{K_\perp}{8\pi^{1/2}M}[-ig\rho^2 y\\
&\qquad+(6+\rho)y(fx-iy)+4i\rho^2]e^{-\rho/2}\,,\\
\chi_b^{(1)}&=\frac{K_\perp}{4(2\pi)^{1/2}M}[-f\rho^2 y+ig(6+\rho)xy]e^{-\rho/2}\,,\\
\chi_c^{(1)}&=\frac{K_\perp}{8\pi^{1/2}M}[ig\rho^2 y\\
&\qquad-(6+\rho)y(fx+iy)+4i\rho^2]e^{-\rho/2}\,,\\
\chi_d^{(1)}&=\frac{K_\perp}{4(2\pi)^{1/2}M}(6+\rho)yze^{-\rho/2}\,.
\end{aligned}\tag{4.75}$$

The first-order functions for b and d are orthogonal to their respective zeroth-order functions, but $\chi_a^{(1)}$ and $\chi_c^{(1)}$ are not, and have been chosen simply to have the least number of terms in the coordinates ρ, x, and y.

As presented, we have had *atomic hydrogen* in mind. According to Eq. (4.44), this leads to a value for $\beta=(m_2-m_1)/2M$ of approximately $\frac{1}{2}$. However, the preceding is applicable to arbitrary mass ratios, and may just as well be used for *positronium,* for which $m_1=m_2$ and $\beta=0$. In this case, the Stark limit

$$\begin{aligned}
f&\to 0\,,\\
g&\to 1\,,\\
\nu&\to 3K_\perp/M\,,
\end{aligned}\tag{4.76}$$

is always obtained for nonzero $K_\perp$. Note, though, that

our treatment neglects $h^{(2)}$, which can be important unless $K_\perp/M \gg \gamma$.

D. Expectation value of the mechanical momentum for a two-body system in a magnetic field

The results just obtained can now be used to evaluate approximately the matrix element over the dipole moment in Eq. (4.15). Converting to atomic units, we have

$$\langle \underline{\Pi}_\perp \rangle = \underline{K}_\perp + \langle \underline{\gamma} \times \underline{\rho} \rangle \ . \tag{4.77}$$

The last term can be expanded in powers of γ according to

$$\langle \underline{\gamma} \times \underline{\rho} \rangle = \frac{\sum_{i,j} \gamma^{i+j} \langle \chi^{(i)} | \underline{\gamma} \times \underline{\rho} | \chi^{(j)} \rangle}{\sum_{i,j} \gamma^{i+j} \langle \chi^{(i)} | \chi^{(j)} \rangle} \ . \tag{4.78}$$

Retaining only terms through second order, the wave functions in Eqs. (4.63), (4.65), (4.68), and (4.75) yield the results

$$n=1: \ \langle \underline{\Pi}_\perp \rangle = \underline{K}_\perp \left[1 - \frac{9}{2M} \gamma^2 \right] ; \tag{4.79}$$

$$\begin{aligned} n=2: \ \langle \underline{\Pi}_\perp \rangle_a &= \underline{K}_\perp \left[1 - \frac{9}{M\nu} \gamma - \frac{24}{M} (8-g^2) \gamma^2 \right] , \\ \langle \underline{\Pi}_\perp \rangle_b &= \underline{K}_\perp \left[1 - \frac{12}{M} (25-12g^2) \gamma^2 \right] , \\ \langle \underline{\Pi}_\perp \rangle_c &= \underline{K}_\perp \left[1 + \frac{9}{M\nu} \gamma - \frac{24}{M} (8-g^2) \gamma^2 \right] , \\ \langle \underline{\Pi}_\perp \rangle_d &= \underline{K}_\perp \left[1 - \frac{156}{M} \gamma^2 \right] . \end{aligned} \tag{4.80}$$

In each case, we have

$$\langle \underline{\Pi}_\perp \rangle = \underline{K}_\perp (1-A) \ , \tag{4.81}$$

where A is a constant depending upon γ and the state under consideration, as well as upon $K_\perp$ itself.

The point here is that, if one wants to properly eliminate the CM degrees of freedom, the energy levels are calculated as functions of the pseudomomentum eigenvalue $\underline{K}_\perp$, for which a clear-cut physical significance seems illusory when both internal and external fields are present. Nevertheless, if B is weak, we can relate $\underline{K}_\perp$ state-by-state to the (measurable) average transverse velocity of the CM, as in Eq. (4.81).

Note that the factor $\frac{9}{2}$ in Eq. (4.79) is the familiar ground-state static (DC) Stark polarizability. In the Stark limit $g \to 1$ [see Eqs. (4.76)], the $n=2$ coefficients of γ^2/M become, in order, 168, 156, 168, and 156, which are the corresponding static polarizabilities for this level. For atomic hydrogen, $M \cong 2\times 10^3$ and $B_0 = 2.35\times 10^9$ G. Therefore, for $B \cong 10^5$ G ($\gamma \cong 4\times 10^{-5}$), which is quite large by usual standards, the *ground-state correction factor* is about

$$A = \frac{9}{2M} \gamma^2 \cong 4\times 10^{-12} \ . \tag{4.82}$$

This is totally negligible compared to unity. For $n=2$, the terms quadratic in γ are larger, since the polarizabilities are about 1.5 orders of magnitude greater, but are still of no significance.

For states a and c, it is evident that A will be much larger in magnitude due to the terms linear in γ. (Note that, as opposed to the model problem with harmonic interaction, the constant of proportionality is larger than unity for state c.) This occurs because the corresponding expectation values of $\underline{\mathscr{g}}$ do not vanish in zeroth order, which is essentially the linear Stark effect (Bethe and Salpeter, 1957). For the Zeeman limit $3K_\perp/M \ll \beta \cong 1/2$, and for a field of 10^5 G again,

$$|A| \cong \frac{9\gamma}{M\nu} \cong \frac{9\gamma}{M\beta} \cong 4\times 10^{-7} \ . \tag{4.83}$$

This is 5 orders of magnitude larger than A for the ground state, but is still small compared to unity. In the Stark limit $3K_\perp/M \gg \frac{1}{2}$,

$$|A| \cong \frac{9\gamma}{M\nu} \cong \frac{3\gamma}{K_\perp} \ , \tag{4.84}$$

so that

$$\langle \underline{\Pi}_\perp \rangle_{\substack{a \\ c}} \cong \underline{K}_\perp \left[1 \mp \frac{3\gamma}{K_\perp} \right] = \underline{K}_\perp \mp 3\gamma \underline{K}_\perp / K_\perp \ . \tag{4.85}$$

The last term is by assumption insignificant compared to the first for any laboratory-size magnetic field. It is interesting, however, that it is independent of the magnitude of $K_\perp$.

E. Discussion of results

These results serve as a quantitative justification (within the nonrelativistic approximation) for ignoring the discrepancy between $\langle \underline{\Pi}_\perp \rangle$ and $\underline{K}_\perp$ for the low-lying states of typical molecular systems in a magnetic field of any reasonable strength. There are some situations which merit further investigations, however.

For positronium, $\beta = 0$ and Eq. (4.85) always applies as long as our neglect of $h^{(2)}$ relative to $h^{(1)}$ remains justified. This requires that $K_\perp \gg \gamma$, which restriction ensures that $\underline{K}_\perp$ is still the dominant term on the right side of Eq. (4.85), but possibly only by a couple of orders of magnitude. This should be examined in a more complete analysis. For the ground state, there is only one zeroth-order function in any event, and we see that A becomes enhanced for two reasons. The more important is that $M=4$ here (in units of the reduced mass) instead of 2×10^3. The other reason is that, from the text following Eq. (4.44), the unit of magnetic intensity, B_0, is reduced by nearly a factor of 4. These two effects conspire to make γ^2/M approximately 8×10^3 larger than in hydrogen for the same value of B. Thus, for $n=1$, $A = 3\times 10^{-8}$ instead of 4×10^{-12}.

For *B large enough* (say, 10^{11}–10^{12} G, as expected in

the neighborhood of neutron stars) that the magnetic field dominates over the Coulomb interaction, it was shown by Wunner, Ruder, and Herold (1980) and Herold, Ruder, and Wunner (1981) that the effects on the energy levels of finite nuclear mass are sometimes comparable to those of the Coulomb binding. The latter paper gives a detailed discussion of computational methods for a two-body neutral system with nonzero $K_\perp$ and strong B. In this extreme, the zeroth-order approximation describes the transverse relative motion with a wave function like the magnetic field wave functions of Sec. II.D.2, and the Coulomb term is treated as a perturbing-coupling potential (see, for instance, the reference sections of Garstang, 1977; Avron, Herbst, and Simon, 1979; Starace and Webster, 1979; and Herold, Ruder, and Wunner, 1981). It would be interesting to see the corresponding first-order wave functions determined, since this would allow approximate evaluation of Eq. (4.15) in a regime complementary to the one we have been considering. (The expectation value $\langle \underline{\Pi}_\perp \rangle$ vanishes for strong fields in zeroth order, i.e., when the particle interaction is neglected, just as for the $\omega_0=0$ limit of the problem in Sec. IV.B.)

For states of higher principal quantum number n, where the nucleus and the electron spend a great deal of time far apart, even the effects of easily attainable fields can be comparable to the average Coulomb interaction. For such states, both linear and quadratic Stark shifts become significantly larger, and this indicates that $\langle \underline{\Pi}_\perp \rangle$ and $\underline{K}_\perp$ may differ much more noticeably. (However, the importance of the diamagnetic term $h^{(2)}$ also grows rapidly with n and must therefore be included.) It would seem very worthwhile to investigate the importance of this question for states of higher n, especially since these are used as prototypes for interpreting experiments involving electrons in high Rydberg states in the presence of an external magnetic field. (See, for example, the reference sections of Garstang, 1977; Starace and Webster, 1979; Panock *et al.*, 1980b; and Rau, 1980. For nonhydrogenic atoms, interaction of the electron with the core can remove the extra degeneracy and suppress the terms in the constant A that are linear in γ.) It has been shown recently that the associated motional electric field can be a major influence for light atoms such as helium (Panock *et al.*, 1980a, 1980b) and lithium (Crosswhite *et al.*, 1979).

We point out that the *linear terms* in A can also be expected if the rigid-rotor approximation is made for a *polyatomic symmetric top molecule with a permanent dipole moment.* The symmetric top eigenfunctions are labeled by the total nuclear angular momentum J, and by space- and body-fixed projections M and K, respectively (not to be confused with the M and K used elsewhere in this paper). Since these states are degenerate with respect to the sign of K, they give rise to a linear Stark effect (have a permanent dipole moment) like that of hydrogen (Townes and Schawlow, 1975). Thus, in a Born-Oppenheimer development, the expectation value of the nuclear part of the dipole moment can be nonzero in zeroth order, leading to terms in A linear in γ just as for the hydrogenic states a and c in Eq. (4.80).

V. CHARGED N-PARTICLE SYSTEMS IN CONSTANT $\underline{E}$ AND $\underline{B}$

A. Wave functions for $E_\perp \neq 0$

Unlike the neutral case, there is no exact means of separating all of the CM degrees of freedom for a charged system when a magnetic field is present. Because the effect upon the energy levels is expected to be quite small there does not appear ever to have been an adequate formulation of how this coupling may be consistently incorporated into calculations. This is the main concern of the first two subsections. After that, we specialize again to the lowest states of a charged two-body system in a magnetic field, presenting perturbative results which are then compared to those obtained in the corresponding one-body calculations of the infinite-nuclear-mass approximation. Since the *spin interaction with the magnetic field* adds only constant shifts to the energy, it is again neglected.

The coupling may be restricted to one CM degree of freedom. First of all, the Hamiltonian H in Eq. (3.40) decomposes into

$$H = H_{||} + \mathscr{H} , \tag{5.1}$$

$$H_{||} = \frac{P_z^2}{2M} - eE_{||}Z , \tag{5.2}$$

$$\mathscr{H} = \frac{\underline{\Pi}_\perp^2}{2M} - e\underline{E}_\perp \cdot \underline{R}_\perp + T_r + V - \underline{\mu}\cdot\underline{E} , \tag{5.3}$$

where, from Eqs. (3.38) and (3.39),

$$\underline{\Pi}_\perp = \underline{P}_\perp - \frac{e}{2c}\underline{B}\times\underline{R}_\perp - \frac{1}{c}\underline{B}\times\underline{\mu} , \tag{5.4}$$

$$T_r = \sum_{i=1}^{N-1} \frac{1}{2a_i}\left[\underline{P}_i - \sum_{j=1}^{N-1}\frac{\epsilon_{ij}}{2c}\underline{B}\times\underline{R}_j\right]^2 . \tag{5.5}$$

The stationary states $\psi_{||}(Z)$ of $H_{||}$ (with $E_{||}\neq 0$) were discussed in Sec. II.D.1. Thus Z is dispensed with immediately and we are left with $\mathscr{H}$, which refers only to X and Y and their conjugate momenta.

Upon boosting the reduced Hamiltonian $\mathscr{H}$ to the drift frame as described in Sec. III.D, we obtain

$$\mathscr{H}_U = \frac{\underline{\Pi}_\perp^2}{2M} + T_r + V - \mu_z E_{||} . \tag{5.6}$$

This Hamiltonian has the two noncommuting constants of motion $\mathscr{K}_x^0$ and $\mathscr{K}_y^0$, which were discussed at length in Sec. II. Exactly as for the single particle, one operator formed out of these two may be diagonalized at the same time as $\mathscr{H}_U$. In this way, one more CM degree of freedom is eliminated. The particular choice made in the drift frame is arbitrary. However, as demonstrated in Sec. II.E, diagonalization of $\mathscr{K}_y^0$ or of $(\mathscr{K}_y^0)^2+(\mathscr{K}_y^0)^2$, followed by a boost back from the drift frame, results in lab-frame solutions which are eigenfunctions of $\mathscr{K}_y$ or of $\mathscr{K}_x^2+\mathscr{K}_y^2$, respectively. Since

$$\mathscr{K}_y = P_y + M\omega X/2 - eE_\perp t$$

is explicitly time dependent, these solution are therefore not stationary states. *Only eigenfunctions of $\mathscr{H}_x^0$ in the drift frame correspond to stationary states in the lab frame.*

Restricting attention to the eigenfunctions of $\mathscr{H}_x^0$, it is necessary to consider only the time-independent wave functions, which satisfy

$$(\mathscr{H}_x^0-\hbar K_x)\psi_{K_xU}=0\,, \tag{5.7}$$

$$(\mathscr{H}_U-\mathscr{E}_d)\psi_{K_xU}=0\,. \tag{5.8}$$

The first of these equations is satisfied by

$$\psi_{K_xU}(\underline{R}_1\cdots\underline{R}_{N-1},\underline{R}_\perp)=\exp\left[iX\left[K_x+\frac{M\omega}{2\hbar}Y\right]\right]\chi_{K_x}(\underline{R}_1\cdots\underline{R}_{N-1},Y)\,. \tag{5.9}$$

The reduced function χ_{K_x} depends upon Y, the CM coordinate in the direction of $\underline{E}_\perp$. Inserting Eqs. (5.6) and (5.9) into (5.8), we find that χ_{K_x} must obey

$$\left[\frac{1}{2M}[(\hbar K_x+M\omega Y+B\mu_y/c)^2+(P_y-B\mu_x/c)^2]+T_r+V-\mu_zE_{||}-\mathscr{E}_d\right]\chi_{K_x}=0\,. \tag{5.10}$$

It is to be observed that the energy in the drift frame, $\mathscr{E}_d$, has no dependence upon K_x. Shifting the origin of Y,

$$Y'=Y+\frac{\hbar K_x}{M\omega}=Y-Y_c\,, \tag{5.11}$$

and defining

$$\chi'_{K_x}(\underline{R}_1\cdots\underline{R}_{N-1},Y')=\chi_{K_x}(\underline{R}_1\cdots\underline{R}_{N-1},Y)\,, \tag{5.12}$$

we simplify Eq. (5.10) to

$$\left[\frac{1}{2M}[(M\omega Y'+B\mu_y/c)^2+(P_y'-B\mu_x/c)^2]+T_r+V-\mu_zE_{||}-\mathscr{E}_d\right]\chi'_{K_x}=0\,. \tag{5.13}$$

Since the eigenvalue equation is not explicitly dependent upon K_x, it follows that $\mathscr{E}_d$ is completely independent of K_x as well. (It should be mentioned that there are no strictly bound states if $E_{||}\neq 0$, since $-\mu_zE_{||}$ approaches $-\infty$ as μ_z approaches $+\infty$, and so ionization, or Stark tunneling, may occur along the z axis.) This is directly related to the proof by Avron, Herbst, and Simon (1978) that the spectrum of a charged N-particle system in a magnetic field is of infinite multiplicity; that is, the well-known Landau degeneracy of a single particle also occurs for charged composite systems. Note that the simple demonstration in Eqs. (5.11)–(5.13) depends upon the fact that e (hence ω) is not zero.

The time-independent wave function in the lab frame is now

$$\psi_{K_x}=\exp[iMv_dX/\hbar]\psi_{K_xU}=\exp\left[iX\left[K_x+\frac{Mv_d}{\hbar}+\frac{M\omega}{2\hbar}Y\right]\right]\chi_{K_x}\,, \tag{5.14}$$

and satisfies

$$(\mathscr{H}_x-\hbar K_x)\psi_{K_x}=0\,, \tag{5.15}$$

$$(\mathscr{H}-\mathscr{E}_l)\psi_{K_x}=0\,, \tag{5.16}$$

where $\mathscr{H}$ is given in Eq. (5.3) and the lab-frame energy is

$$\mathscr{E}_l=\mathscr{E}_d+\hbar K_xv_d+\tfrac{1}{2}Mv_d^2\,. \tag{5.17}$$

Exactly as for the single particle [see Eqs. (2.20) and (2.88)], the only dependence of $\mathscr{E}_l$ upon K_x is in the second term. For small B, K_x may be related to $\langle\Pi_x\rangle$ analogously to the treatment of Sec. IV. This requires integration over Y as well as the internal coordinates.

The full solution including the Z dependence is thus

$$\psi=\psi_{||}\psi_{K_x}=\psi_{||}(Z)\exp\left[iX\left[K_x+\frac{Mv_d}{\hbar}+\frac{M\omega}{2\hbar}Y\right]\right]\chi_{K_x} \tag{5.18}$$

in the multipolar gauge, and

$$\psi_{\rm mc}=U_{\rm PZW}^\dagger\psi=\psi_{||}(Z)\exp\left[\frac{i}{2\hbar c}\underline{B}\cdot\underline{R}\times\underline{\mu}+iX\left[K_x+\frac{Mv_d}{\hbar}+\frac{M\omega}{2\hbar}Y\right]\right]\chi_{K_x} \tag{5.19}$$

in the minimally coupled representation. Here $\psi_{||}(Z)$ is either a plane wave or the Airy-function solution of Eq. (2.51), depending on whether or not $E_{||}=0$.

It is clear that all of the information about the internal dynamics is contained solely in the drift-frame energy $\mathscr{E}_d$, which may in principle be determined from Eq. (5.10) or (5.13). As mentioned above, however, there are different choices for the coupled CM coordinate possible in the drift frame, all of which will give the same $\mathscr{E}_d$ obtained by using Y. In the following, we use an alternative but equivalent choice.

B. Drift-frame eigenfunctions

We now turn to an examination of the time-independent drift-frame eigenfunctions of $\mathscr{H}_U$ and $(\underline{K}_\perp^0)^2$. It was brought out by Avron, Herbst, and Simon (1978) that this is a natural basis for N-particle Hamiltonians with $E_\perp=0$. Although these functions can be boosted to a frame with $E_\perp\neq 0$, the resulting solutions would be explicitly time dependent [cf. Eq. (2.90)] and are not of concern here.

The total transverse mechanical momentum may be written as

$$\underline{\Pi}_\perp=\underline{\Pi}_{s\perp}-\frac{1}{c}\underline{B}\times\underline{\mu}\ , \tag{5.20}$$

where $\underline{\Pi}_{s\perp}$ is the single-particle version

$$\underline{\Pi}_{s\perp}=\underline{P}_\perp-\frac{e}{2c}\underline{B}\times\underline{R}_\perp\ . \tag{5.21}$$

By expanding the CM kinetic energy, the drift-frame Hamiltonian $\mathscr{H}_U$ can be divided into three terms,

$$\begin{aligned}\mathscr{H}_U&=\frac{1}{2M}\Pi_\perp^2+T_r+V-\mu_z E_{||}\\&=\mathscr{H}_r+\mathscr{H}_s+\mathscr{H}_{rs}\ ,\end{aligned} \tag{5.22}$$

where

$$\mathscr{H}_r=T_r+V-\mu_z E_{||}+\frac{1}{2Mc^2}(\underline{B}\times\underline{\mu})^2\ , \tag{5.23}$$

$$\mathscr{H}_s=\frac{1}{2M}\Pi_{s\perp}^2=\hbar\,|\,\omega\,|\,(a^\dagger a+\tfrac{1}{2})\ , \tag{5.24}$$

and

$$\begin{aligned}\mathscr{H}_{rs}&=-\frac{1}{Mc}\underline{\Pi}_{s\perp}\cdot\underline{B}\times\underline{\mu}\\&=\frac{\sigma}{M}\left[\frac{|\,e\,|\hbar B^3}{2c^3}\right]^{1/2}(\mu_{-\sigma}a+\mu_{+\sigma}a^\dagger)\ .\end{aligned} \tag{5.25}$$

The annihilation and creation operators a and $a^\dagger$ were defined as linear combinations of Π_{sx} and Π_{sy} in Eqs. (2.65), and also by

$$\begin{aligned}a&=\frac{\partial}{\partial W^*}+\frac{1}{2}W\ ,\\a^\dagger&=-\frac{\partial}{\partial W}+\frac{1}{2}W^*\ ,\end{aligned} \tag{5.26}$$

where

$$W=\frac{X+i\sigma Y}{\sqrt{2}\lambda}\ , \tag{5.27}$$

and λ is the cyclotron radius $(\hbar c/|\,e\,|B)^{1/2}$ ties $\mu_\pm$ are

$$\mu_\pm=\mu_x\pm i\mu_y\ . \tag{5.28}$$

It has already been mentioned [see Eqs. (3.17) and (3.47)] that $\mathscr{H}_U$ has another constant of the motion, the z component of the total canonical angular momentum about the origin,

$$L_{tz}=L_{rz}+L_{sz}\ , \tag{5.29}$$

where

$$L_{rz}=\sum_{i=1}^{N-1}(X_iP_{iy}-Y_iP_{ix}) \tag{5.30}$$

and

$$\begin{aligned}L_{sz}&=XP_y-YP_x\\&=\sigma\hbar(b^\dagger b-a^\dagger a)\ .\end{aligned} \tag{5.31}$$

The last form for L_{sz} is from Eq. (2.68) and involves the annihilation and creation operators b and $b^\dagger$ given in Eqs. (2.65) as linear combinations of K_x^0 and K_y^0. In terms of W and W^*, they are

$$\begin{aligned}b&=\frac{\partial}{\partial W}+\frac{1}{2}W^*\ ,\\b^\dagger&=-\frac{\partial}{\partial W^*}+\frac{1}{2}W\ .\end{aligned} \tag{5.32}$$

The division of L_{tz} into L_{rz} and L_{sz} is useful in the absence of $\underline{B}$, since they are then separately conserved and mutually commuting. With regard to the Hamiltonian $\mathscr{H}_U$, however, they both commute with $\mathscr{H}_r$ and $\mathscr{H}_s$, but only their *sum* commutes with the coupling terms in $\mathscr{H}_{rs}$.

On the other hand, L_{tz} may still be written in terms of two mutually commuting constants of the motion

$$L_{tz}=\mathscr{L}_2-\mathscr{L}_1\ , \tag{5.33}$$

where

$$\mathscr{L}_1=\sigma\hbar a^\dagger a-L_{rz} \tag{5.34}$$

and

$$\mathscr{L}_2=\sigma\hbar b^\dagger b\ . \tag{5.35}$$

Diagonalization of $\mathscr{L}_2$ corresponds to the previously mentioned diagonalization of $(\underline{K}_1^0)^2$. Taking the wave function as a simultaneous eigenfunction of $\mathscr{L}_1$ and $\mathscr{L}_2$ is then the same thing as quantizing the z component of the total canonical angular momentum about the origin. This is the analog of the single-particle angular momentum basis of Sec. II.D.2.

Thus it is required that ψ (where the subscript U is suppressed, as is the d on $\mathscr{E}_d$) be a simultaneous eigenfunction of three operators,

$$(\mathscr{H}_U-\mathscr{E})\psi=0\ , \tag{5.36}$$

$$(\mathscr{L}_1-\sigma p\hbar)\psi=0\ , \tag{5.37}$$

$$(\mathscr{L}_2-\sigma n_2\hbar)\psi=0\ . \tag{5.38}$$

The eigenvalue of $\mathscr{L}_2$ is obtained from Eq. (2.70), with n_2 assuming the values $0,1,2,\ldots$. The energy is independent of n_2, since b and $b^\dagger$ do not appear in the Hamiltonian. The operator $a^\dagger a$ similarly has the eigenvalue $n_1=0,1,2,\ldots$, but n_1 is not a good quantum number here. In its place, we have the eigenvalue σph of $\mathscr{L}_1$, where p can be a positive or negative integer or zero (see Secs. V.C and V.D).

The simplest situation occurs when $n_2=0$, since then ψ can be taken to be a solution of

$$b\psi=\left[\frac{\partial}{\partial W}+\frac{1}{2}W^*\right]\psi=0\ . \tag{5.39}$$

This equation is satisfied by

$$\psi=\exp(-\tfrac{1}{2}\,|\,W\,|^2)f(\underline{R}_1\cdots\underline{R}_{N-1},W^*)\ . \tag{5.40}$$

If this is inserted into Eqs. (5.36) and (5.37), we obtain

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$$\left[\mathscr{H}_r+\hbar\omega\left[W^*\frac{\partial}{\partial W^*}+\frac{1}{2}\right]+\frac{\sigma}{M}\left[\frac{|e|\hbar B^3}{2c^3}\right]^{1/2}\left[\mu_{-\sigma}\frac{\partial}{\partial W^*}+\mu_\sigma W^*\right]-\mathscr{E}\right]f=0\,, \tag{5.41}$$

$$\left[\sigma\hbar W^*\frac{\partial}{\partial W^*}-L_{rz}-\sigma p\hbar\right]f=0\,, \tag{5.42}$$

which may be combined to eliminate $W^*(\partial/\partial W^*)$. Once f has been determined, eigenfunctions for higher n_2 can be obtained by repeated application of $b^\dagger$ from Eq. (5.32), in analogy to the procedure for the single-particle solutions. Thus it will be sufficient hereafter to consider only $n_2=0$.

One means of solving for f is to expand it in powers of W^*. This is equivalent to expanding the full wave function ψ in terms of the orthonormal $n_2=0$ angular momentum basis states from Eq. (2.74),

$$\psi_{\perp;n_1}(W,W^*)=\psi_{\perp;n_1,n_2=0}$$
$$=(\pi n_1!)^{-1/2}(W^*)^{n_1}\exp(-\tfrac{1}{2}|W|^2)\,. \tag{5.43}$$

These are taken to be normalized in W and W^* instead of X and Y, which involves deleting a factor of only $1/\sqrt{2}\lambda$ from the previous definition. The full wave function is thus

$$\psi_p=\sum_{n_1=0}^{\infty}\psi_{\perp;n_1}(W,W^*)\chi_{p,\sigma n_1-\sigma p}(\underline{R}_1\cdots\underline{R}_{N-1})\,, \tag{5.44}$$

where the "expansion coefficients" are functions of the internal variables and eigenfunctions of L_{rz},

$$(L_{rz}-m\hbar)\chi_{pm}=0\,. \tag{5.45}$$

Equations (5.37) and (5.38) are then automatically satisfied. Equation (5.44) may now be inserted into Eq. (5.36) to determine the (coupled) equations satisfied by the χ_{pm}. Using Eqs. (2.69), (2.70), and (5.22)—(5.25) and the orthonormality of the $\psi_{\perp;n_1}$, we obtain

$$\left[T_r+V-\mu_z E_{||}+\frac{1}{2Mc^2}(\underline{B}\times\underline{\mu})^2+\hbar|\omega|(n_1+\tfrac{1}{2})-\mathscr{E}_p\right]\chi_{p,\sigma n_1-\sigma p}$$
$$+\frac{\sigma}{M}\left[\frac{|e|\hbar B^3}{2c^3}\right]^{1/2}[(n_1+1)^{1/2}\mu_{-\sigma}\chi_{p,\sigma n_1-\sigma p+\sigma}+n_1^{1/2}\mu_\sigma\chi_{p,\sigma n_1-\sigma p-\sigma}]=0\,. \tag{5.46}$$

These equations, although coupled, involve only internal coordinates. When B is weak and n_1 is not very large, the coupling (of order $B^{3/2}$) is small, and this comes as close as possible to separation of the CM coordinates. Equation (5.46) may be rewritten as a matrix equation

$$(\underline{\underline{h}}-\mathscr{E}_p\underline{\underline{1}})\underline{\chi}_p=(\underline{\underline{h}}^{(0)}+B\underline{\underline{h}}^{(1)}+B^{3/2}\underline{\underline{h}}^{(3/2)}$$
$$+B^2\underline{\underline{h}}^{(2)}-\mathscr{E}_p\underline{\underline{1}})\underline{\chi}_p=0\,. \tag{5.47}$$

The rows and columns are labeled by n_1, $\underline{\chi}_p$ is a column vector,

$$\underline{\chi}_p=(\chi_{p,-\sigma p},\chi_{p,\sigma-\sigma p},\ldots,\chi_{p,\sigma n_1-\sigma p},\ldots)^T\,, \tag{5.48}$$

and all of the matrices except $\underline{\underline{h}}^{(3/2)}$ are diagonal. The exact forms of these matrices can be obtained from Eq. (5.46) and the definition of T_r in Eq. (3.39), but are not important here.

Up until this point, no approximations have been made. A perturbation expansion of $\mathscr{E}_p$ and $\underline{\chi}_p$ with $B^{1/2}$ as the expansion parameter is naturally suggested. We restrict discussion to positively charged ions and vanishing $E_{||}$ for simplicity. The zeroth-order equation is then

$$\left[\sum_{i=1}^{N-1}\frac{1}{2a_i}P_i^2+V-\mathscr{E}_p^{(0)}\right]\chi_{pm}^{(0)}=0\,, \tag{5.49}$$

which is simply the usual field-free eigenvalue equation after separation of the CM.

Equation (5.49) indicates that we may take as our zeroth-order total wave function just one component in the expansion of Eq. (5.44),

$$\psi_p^{(0)}=\psi_{\perp;n_1}\chi_{p,n_1-p}^{(0)}\,. \tag{5.50}$$

This means that the state under consideration emanates from a particular angular momentum state for the CM and a particular field-free internal state. This is reasonable, since the CM motion should for the most part be that of a single charge particle with no dipole or higher multipole moments (see Appendix A). Note that, in terms of X and Y, $\psi_{\perp;n_1}$ depends explicitly upon B through the cyclotron radius. This is merely a formality, since $\psi_p^{(0)}$ can be considered to be the zeroth-order wave function for the modified problem in which the scaled coordinates W and W^* are used. In terms of these, $\psi_{\perp;n_1}$ is explicitly independent of B.

The reader may have noticed the formal analogy between the Hamiltonian $\mathscr{H}_U$ in Eqs. (5.22)—(5.25) and the Fock-Schrödinger Hamiltonian for a molecular system interacting with a single mode of a quantized radiation field (with correspondences $\mathscr{H}_r\leftrightarrow H_{\text{matter}}$, $\mathscr{H}_s\leftrightarrow H_{\text{field}}$, and $\mathscr{H}_{rs}\leftrightarrow H_{\text{interaction}}$). The form of $\psi_p^{(0)}$ in Eq. (5.50) then

resembles the common choice for the latter problem of a zeroth-order function consisting of a product of unperturbed field and matter states. To complete the analogy, however, $\chi^{(0)}_{pm}$ would have to be replaced by a simultaneous eigenfunction of $\mathscr{H}_r$ and L_{rz}.

We remark that, if the field-free internal states in Eq. (5.49) have only rotational degeneracy (in m), then the coupling terms involving the dipole moment will not contribute to the energy until order B^3. This is ultimately for the same reason (parity arguments) that such systems exhibit a quadratic Stark shift, but not a linear one, in the presence of a static electric field (Bethe and Salpeter, 1957). On the other hand, a higher degeneracy such as in the excited states of hydrogenic ions complicates the situtation (see Sec. V.D).

For B small enough that perturbation theory is appropriate, the effects of CM motion on any common molecular ion will be quite small. Nevertheless, the foregoing provides a means of including these effects purely within the context of bound-state perturbation theory, as is demonstrated in the following subsections for a two-body ion. In the other extreme, where B is so large that it dominates the interparticle interaction, CM effects may be much more significant if the results for neutral systems (Wunner, Ruder, and Herold, 1980; Herold, Ruder, and Wunner, 1981) are any indication. For this problem, some of the considerations above should prove useful, although one would probably want to scale the internal coordinates by $B^{1/2}$ as well (Avron, Herbst, and Simon, 1979).

The expansion in Eq. (5.44) is particularly convenient if the field-free internal states are to be chosen as eigenfunctions of L_{rz}. An analogous expansion for $\psi_{K_x U}$ of Eq. (5.9) could be made, though, in which case the appropriate single-particle magnetic field wave functions would be the eigenfunctions of $\mathscr{K}^0_x$ given in Eq. (2.56).

C. Two-body ground state in a magnetic field

As an example of the preceding formalism, we present here the perturbed wave functions and energies for the ground state of a positively charged hydrogenic ion ($\sigma>0$) in a magnetic field. The energy is evaluated through $O(B^6)$. This is sufficient for a comparison with the one-body calculations which make use of the infinite-nuclear-mass approximation. The $n=2$ manifold is not considered until Sec. V.D.

1. Perturbation equations

Atomic units are used again,

$$\mu=\hbar=a_0=1\ , \tag{5.51}$$

but we emphasize that these are not the same as the units employed for the neutral system in Sec. IV. Taking particle 1 to have charge $-q$ and particle 2 to have charge Zq, the appropriate first Bohr radius depends upon Z as well as μ,

$$a_0=\frac{\hbar^2}{\mu Z q^2}\ . \tag{5.52}$$

This leads to the unit of energy

$$\mathscr{E}_0=\frac{\hbar^2}{\mu a_0^2}=\frac{\mu Z^2 q^4}{\hbar^2} \tag{5.53}$$

and to a redefined characteristic magnetic intensity

$$B_0=\frac{\hbar c}{q a_0^2}=\frac{\mu^2 Z^2 q^3 c}{\hbar^3}\ . \tag{5.54}$$

With the above definition of the unit of length, the hydrogenic orbitals Φ_{nlm} are of the same form as in the neutral case. The alternative is adoption of the units for a neutral system ($Z=1$), in which event the coordinate $\underset{\sim}{\rho}$ becomes explicitly multiplied by Z everywhere it occurs. The Z-dependent units used here were employed by Surmelian and O'Connell (1974) to exhibit scaling properties of the energy for a single body moving in both a magnetic field and a fixed Coulomb field.

The corresponding version of Eq. (5.47) is, from Appendix B,

$$(\underline{\underline{h}}^{(0)}+\gamma\underline{\underline{h}}^{(1)}+\gamma^{3/2}\underline{\underline{h}}^{(3/2)}+\gamma^2\underline{\underline{h}}^{(2)}-\mathscr{E}_p\underline{\underline{1}})\underline{\chi}_p=0\ , \tag{5.55}$$

where $\underline{\gamma}=\underline{B}/B_0$ and

$$h^{(0)}_{n_1,n_1'}=\delta_{n_1,n_1'}h^{(0)}=\delta_{n_1,n_1'}\left[-\frac{1}{2}\nabla^2-\frac{1}{\rho}\right]\ , \tag{5.56}$$

$$h^{(1)}_{n_1,n_1'}=\delta_{n_1,n_1'}\left[\alpha_1(n_1+\tfrac{1}{2})-i\alpha_2\left[x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right]\right]\ , \tag{5.57}$$

$$h^{(3/2)}_{n_1,n_1'}=-\delta_{n_1',n_1+1}\alpha_3(n_1+1)^{1/2}(x-iy)-\delta_{n_1',n_1-1}\alpha_3 n_1^{1/2}(x+iy)\ , \tag{5.58}$$

$$h^{(2)}_{n_1,n_1'}=\delta_{n_1,n_1'}\frac{\alpha_4}{8}(x^2+y^2)\ . \tag{5.59}$$

The constants introduced here are

$$\alpha_1=\frac{Z-1}{M}\ , \tag{5.60}$$

$$\alpha_2=\frac{1}{2}\frac{1-Z\delta^2}{(1+\delta)^2}\ , \tag{5.61}$$

$$\alpha_3=\frac{1+Z\delta}{M(1+\delta)}\left[\frac{Z-1}{2}\right]^{1/2}\ , \tag{5.62}$$

$$\alpha_4=(1+\delta)^{-4}(1+4\delta+6Z\delta^2+4Z^2\delta^3+Z^2\delta^4)\ , \tag{5.63}$$

where δ is the dimensionless mass ratio

$$\delta=\frac{m_1}{m_2}\ . \tag{5.64}$$

The total mass M in atomic units can also be expressed as $M/\mu=(1+\delta)^2/\delta$.

The energy $\mathscr{E}_p$ and component wave functions χ_{pm} are now expanded in powers of $\gamma^{1/2}$, dropping the subscript p for notational economy,

$$\mathscr{E}=\sum_{i=0}^{\infty}\gamma^{i/2}\mathscr{E}^{(i/2)}, \tag{5.65}$$

$$\chi_m=\sum_{i=0}^{\infty}\gamma^{i/2}\chi_m^{(i/2)}. \tag{5.66}$$

Equation (5.66) is equivalent to an expansion of the column vector $\underline{\chi}_p\equiv\underline{\chi}$,

$$\underline{\chi}=\sum_{i=0}^{\infty}\gamma^{i/2}\underline{\chi}^{(i/2)}, \tag{5.67}$$

where, according to Eq. (5.48),

$$\underline{\chi}=\sum_{m=-p}^{\infty}\underline{e}_{m+p}\chi_m, \tag{5.68}$$

$$\underline{\chi}^{(i/2)}=\sum_{m=-p}^{\infty}\underline{e}_{m+p}\chi_m^{(i/2)}. \tag{5.69}$$

Here $\underline{e}_j$ is a column vector with unity in row j and zeros elsewhere. Expanding Eq. (5.55) with the aid of Eqs. (5.65) and (5.67), the perturbation equations of order $\gamma^{k/2}$ are

$$\sum_{i=0}^{k}(\underline{\underline{h}}^{(i/2)}-\mathscr{E}^{(i/2)}\underline{\underline{1}})\underline{\chi}^{[(k-i)/2]}=0. \tag{5.70}$$

We are assuming here that the zeroth-order state, represented by $\underline{\chi}^{(0)}$, is nondegenerate.

These equations can be solved by the conventional Rayleigh-Schrödinger procedure. At the kth step, we know all $\mathscr{E}^{(i/2)}$ and $\underline{\chi}^{(i/2)}$ for $i<k$. Then $\mathscr{E}^{(k/2)}$ is determined by multiplying Eq. (5.70) by $\underline{\chi}^{(0)\dagger}$, which is normalized to unity, and integrating,

$$\mathscr{E}^{(k/2)}=\langle\underline{\chi}^{(0)}\,|\,\underline{\underline{h}}^{(k/2)}\,|\,\underline{\chi}^{(0)}\rangle+\sum_{i=1}^{k-1}\langle\underline{\chi}^{(0)}\,|\,(\underline{\underline{h}}^{(i/2)}-\mathscr{E}^{(i/2)}\underline{\underline{1}})\,|\,\underline{\chi}^{[(k-i)/2]}\rangle. \tag{5.71}$$

The matrix elements are defined by, for any operator $\underline{\underline{\mathscr{O}}}$,

$$\langle\underline{\chi}^{(i/2)}\,|\,\underline{\underline{\mathscr{O}}}\,|\,\underline{\chi}^{(j/2)}\rangle=\int d\underline{\kappa}\,\underline{\chi}^{(i/2)\dagger}\underline{\underline{\mathscr{O}}}\,\underline{\chi}^{(j/2)}. \tag{5.72}$$

The $i=0$ term in Eq. (5.71) has dropped out, as usual, by virtue of the zeroth-order equation and the hermiticity of $h^{(0)}$. With $\mathscr{E}^{(k/2)}$ known, $\underline{\chi}^{(k/2)}$ is obtained as a solution of the inhomogeneous differential equation

$$(h^{(0)}-\mathscr{E}^{(0)})\underline{\chi}^{(k/2)}=-\sum_{i=1}^{k}(\underline{\underline{h}}^{(i/2)}-\chi^{(i/2)}\underline{\underline{1}})\underline{\chi}^{[(k-i)/2]}, \tag{5.73}$$

where all quantities on the right side have been previously determined. The component equations here are all of the same general nature as those in the usual perturbation treatments (e.g., Sec. IV.C), and may be solved by the same means.[10]

2. Perturbed wave functions

We now specialize to the ground state and take $\underline{\chi}^{(0)}$ to consist of the single component

$$\underline{\chi}^{(0)}=\underline{e}_{n_1}\Phi_{100}=\underline{e}_{n_1}\pi^{-1/2}e^{-\kappa}, \tag{5.74}$$

and

$$\mathscr{E}^{(0)}=-\tfrac{1}{2}. \tag{5.75}$$

According to Eq. (5.50), this corresponds to describing the CM in zeroth order by $\psi_{\perp;n_1}(W,W^*)$ of Eq. (5.43). The eigenvalue p is given by (since $m=0$)

$$p=n_1-m=n_1. \tag{5.76}$$

Just as in Sec. IV, all components $\chi_m^{(i/2)}$ are of the form

$$\chi_m^{(i/2)}=\pi^{-1/2}F_m^{(i/2)}(\underline{\kappa})e^{-\kappa}, \tag{5.77}$$

where $F_m^{(i/2)}$ is a polynomial in the coordinates. The similarity transformation of Eq. (4.60),

$$\bar{\eta}_1^{(0)}=e^{\kappa}(h^{(0)}-\mathscr{E}^{(0)})e^{-\kappa}, \tag{5.78}$$

can be used to strip away the exponential from Eqs. (5.73), in analogy to Eq. (4.61). The most convenient coordinates to use in this case are κ, u, and u^*, where

$$u=x+iy,\qquad u^*=x-iy. \tag{5.79}$$

We again eschew details, but mention that systematic solution of the transformed inhomogeneous equations is simplified by the relation

$$\bar{\eta}_1^{(0)}\kappa^j u^k u^{*l}=(j+k+l)\kappa^{j-1}u^k u^{*l}-\frac{j(j+1+2k+2l)}{2}\kappa^{j-2}u^k u^{*l}-2kl\kappa^j u^{k-1}u^{*l-1}. \tag{5.80}$$

Through order γ^4, or $i=8$, the column vectors $\underline{\chi}^{(i/2)}$

[10] Also in analogy to the usual treatments of, say, the Zeeman effect for infinite nuclear mass, the energy series is only expected to be asymptotic. The possibility arises that the Zeeman problem *with the CM included* could be treated by the summation methods currently used in divergent perturbation problems. See, for example, Int. J. Quantum Chem. 21, issue 1 (Jan. 1982), which contains the proceedings of a workshop on perturbation theory of large order.

have the form

$$\begin{aligned}
&\underline{\chi}^{(0)}=\underline{e}_{n_1}\chi_0^{(0)}\,,\\
&\underline{\chi}^{(1/2)}=0\,,\\
&\underline{\chi}^{(1)}=0\,,\\
&\underline{\chi}^{(3/2)}=\underline{e}_{p-1}\chi_{-1}^{(3/2)}+\underline{e}_{p+1}\chi_1^{(3/2)}\,,\\
&\underline{\chi}^{(2)}=\underline{e}_p\chi_0^{(2)}\,,\\
&\underline{\chi}^{(5/2)}=\underline{e}_{p-1}\chi_{-1}^{(5/2)}+\underline{e}_{p+1}\chi_1^{(5/2)}\,,\\
&\underline{\chi}^{(3)}=\underline{e}_{p-2}\chi_{-2}^{(3)}+\underline{e}_p\chi_0^{(3)}+\underline{e}_{p+2}\chi_2^{(3)}\,,\\
&\underline{\chi}^{(7/2)}=\underline{e}_{p-1}\chi_{-1}^{(7/2)}+\underline{e}_{p+1}\chi_1^{(7/2)}\,,\\
&\underline{\chi}^{(4)}=\underline{e}_{p-2}\chi_{-2}^{(4)}+\underline{e}_p\chi_0^{(4)}+\underline{e}_{p+2}\chi_2^{(4)}\,.
\end{aligned}\tag{5.81}$$

The polynomials $F_m^{(i/2)}$ of the component functions are listed in Table I. Using these results in conjuction with Eqs. (5.43) and (5.44), the corresponding orders of the full wave function $\psi(\kappa,u,u^*,W,W^*)$ are obtained:

$$\psi=\sum_{i=0}^{\infty}\gamma^{i/2}\psi^{(i/2)}\,,\tag{5.82}$$

$$\psi^{(0)}=\psi_{\perp;p}\chi_0^{(0)}\,,$$

$$\psi^{(3/2)}=\psi_{\perp;p-1}\chi_{-1}^{(3/2)}+\psi_{\perp;p+1}\chi_1^{(3/2)},\ \text{etc.}\tag{5.83}$$

The polynomials $G^{(i/2)}$, defined by

$$\psi^{(i/2)}=\pi^{-1}(p!)^{-1/2}G^{(i/2)}(\kappa,u,u^*,W,W^*)\times\exp\left[-\frac{|W|^2}{2}-\kappa\right],\tag{5.84}$$

are given in Table II. No particular normalization condition has been imposed beyond minimizing the number of terms (in the variables κ, u, and u^*) in the component functions $\chi_m^{(i/2)}$. We note that, to make $\psi^{(i/2)}$ orthogonal to $\psi^{(0)}$ (intermediate normalization), it is necessary only to make $\chi_0^{(i/2)}$ orthogonal to $\chi_0^{(0)}$.

3. Perturbed energy and comparison with infinite-nuclear-mass limit

The calculation described in Sec. V.C.2 has been directed at obtaining the perturbed eigenvalue $\mathscr{E}$ of $\mathscr{H}_U$ [given by Eq. (5.22) with $E_{||}=0$]. The eigenvalue reduces to the energy of the ground internal state as $\gamma\to 0$, and has the expansion

$$\mathscr{E}=\mathscr{E}_0\sum_{i=0}^{\infty}\gamma^i\mathscr{E}^{(i)}\,,\tag{5.85}$$

where $\gamma=B/B_0$, and B_0 is defined in Eq. (5.54). This expansion differs slightly from the form given in Eq. (5.65). The factor $\mathscr{E}_0$ from Eq. (5.53) has been added to convert $\mathscr{E}$ back to Gaussian units for later convenience. Also, explicit note has been taken of the fact that all energy coefficients of half-integral order vanish,

$$\mathscr{E}^{[(2k+1)/2]}=0\,.\tag{5.86}$$

The integral-order coefficients are listed in the second column of Table III. It should be remembered that the quantum number n_2 can assume the values $0,1,2,\ldots$, and that the results here are applicable to any of these values [cf. the discussion after Eq. (5.38)].

It is interesting to observe how the perturbed energies depend upon the quantum number p which is associated with the CM. The odd-integral orders $\mathscr{E}^{(1)}$, $\mathscr{E}^{(3)}$, and $\mathscr{E}^{(5)}$ are all proportional to $p+\frac{1}{2}$, while the even orders $\mathscr{E}^{(0)}$, $\mathscr{E}^{(2)}$, and $\mathscr{E}^{(4)}$ are independent of p. Thus, through order γ^5, states of adjacent p are equally spaced. We have carried out the energy calculation through order γ^6, where a term proportional to $(p+\frac{1}{2})^2$ appears. Although we have not proceeded further, $\mathscr{E}^{(7)}$ and $\mathscr{E}^{(8)}$ could also be obtained from the wave functions given here (Hirschfelder, Byers Brown, and Esptein, 1964).

Since $\alpha_1\gamma$ is simply $\hbar|\omega|$ expressed in atomic units, the term $\mathscr{E}^{(1)}$ is recognized as the single-particle energy given in Eq. (2.71) [see also Eq. (5.46)]. It is worthwhile to point out that everywhere else the constants α_1 and α_2 appear only in the combination $\alpha_1+\alpha_2$.

Also noteworthy is the fact that α_3, the constant occurring in $\underline{\underline{h}}^{(3/2)}$, enters into the results as α_3^2. For example, the first place it shows up is in $\mathscr{E}^{(3)}$, in line with the statement at the end of Sec. V.B that the coupling between the CM and internal degrees of freedom does not manifest itself until order γ^3. The dependence only on α_3^2 is due to the fact that $\underline{\underline{h}}^{(3/2)}$ couples only component functions χ_m with values of m differing by ± 1. Comparing Eqs. (5.71) and (5.74), it is clear that $\mathscr{E}^{(k/2)}$ depends only upon the $m=0$ (or $n_1=p$) component of Eq. (5.70). Since only terms corresponding to propagating $\underline{\underline{h}}^{(3/2)}$ an even number of times in the perturbation sequence can contribute to this component, none of the energy coefficients can depend upon an odd power of α_3.

An electric field $\underline{E}_{||}$ parallel to $\underline{B}$ can be accommodated by generalizing the treatment in Sec. V.C.1 to that of a double-perturbation problem (Hirschfelder, Byers Brown, and Epstein, 1964). The energy expansion and lowest-order coefficients are

$$\begin{aligned}
&\mathscr{E}=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\gamma^i\left[\frac{1+Z\delta}{1+\delta}\frac{a_0^2}{qZ}E_{||}\right]^{2j}\mathscr{E}^{(i,2j)}\,,\\
&\mathscr{E}^{(0,2)}=-\tfrac{9}{4}\,,\\
&\mathscr{E}^{(0,4)}=-\tfrac{3555}{64}\,,\\
&\mathscr{E}^{(1,2)}=0\,,\\
&\mathscr{E}^{(2,2)}=\tfrac{159}{32}\alpha_4\,.
\end{aligned}\tag{5.87}$$

The energy coefficients $\mathscr{E}^{(i,0)}$ are the same as the $\mathscr{E}^{(i)}$ of Table III. The first Bohr radius a_0 is defined in Eq. (5.52), and the expansion parameter associated with the electric field is obtained from Eqs. (B14), (B16), and (B26). In the energy expansion, we have taken into account not only that the terms of half-integral order in γ vanish, but also that the terms of odd-integral order in the electric field do. The latter event occurs because the elec-

TABLE I. Polynomials $F_m^{(i/2)}$ through $i=8$, as defined in Eq. (5.77). The constants α_1–α_4 are defined in Eqs. (5.60)–(5.63).

$i=0$ $F_0^{(0)}=1$

$i=3$ $F_{-1}^{(3/2)}=\alpha_3(p)^{1/2}u^*\left[1+\frac{\kappa}{2}\right]$

$F_1^{(3/2)}=\alpha_3(p+1)^{1/2}u\left[1+\frac{\kappa}{2}\right]$

$i=4$ $F_0^{(2)}=-\frac{\alpha_4}{24}[uu^*(\frac{3}{2}+\kappa)+\kappa^2]$

$i=5$ $F_{-1}^{(5/2)}=\frac{\alpha_3(\alpha_1+\alpha_2)}{6}(p)^{1/2}u^*f^{(5/2)}$

$F_1^{(5/2)}=-\frac{\alpha_3(\alpha_1+\alpha_2)}{6}(p+1)^{1/2}uf^{(5/2)}$

$f^{(5/2)}(\kappa)=11+\frac{11}{2}\kappa+\kappa^2$

$i=6$ $F_{-2}^{(3)}=\frac{\alpha_3^2}{8}[p(p-1)]^{1/2}u^{*2}f_i^{(3)}$

$F_0^{(3)}=\frac{\alpha_3^2}{8}(2p+1)(uu^*f_i^{(3)}+f_{ii}^{(3)})$

$F_2^{(3)}=\frac{\alpha_3^2}{8}[(p+1)(p+2)]^{1/2}u^2f_i^{(3)}$

$f_i^{(3)}=\frac{15}{2}+5\kappa+\kappa^2$

$f_{ii}^{(3)}=7\kappa^2+\frac{2}{3}\kappa^3$

$i=7$ $F_{-1}^{(7/2)}=\frac{\alpha_3(\alpha_1+\alpha_2)^2}{24}(p)^{1/2}u^*f_i^{(7/2)}-\frac{\alpha_3\alpha_4}{48}(p)^{1/2}(uu^{*2}f_{ii}^{(7/2)}+u^*f_{iii}^{(7/2)})$

$F_1^{(7/2)}=\frac{\alpha_3(\alpha_1+\alpha_2)^2}{24}(p+1)^{1/2}uf_i^{(7/2)}-\frac{\alpha_3\alpha_4}{48}(p+1)^{1/2}(u^2u^*f_{ii}^{(7/2)}+uf_{iii}^{(7/2)})$

$f_i^{(7/2)}=\frac{287}{3}+\frac{287}{6}\kappa+\frac{31}{3}\kappa^2+\kappa^3$

$f_{ii}^{(7/2)}=6+\frac{9}{2}\kappa+\kappa^2$

$f_{iii}^{(7/2)}=\frac{109}{2}+\frac{109}{4}\kappa+\frac{17}{2}\kappa^2+\frac{3}{2}\kappa^3$

$i=8$ $F_{-2}^{(4)}=\frac{\alpha_3^2(\alpha_1+\alpha_2)}{12}[p(p-1)]^{1/2}u^{*2}f_i^{(4)}$

$F_0^{(4)}=-\frac{\alpha_3^2(\alpha_1+\alpha_2)}{30}(uu^*f_{ii}^{(4)}+f_{iii}^{(4)})+\frac{\alpha_4^2}{1152}(u^2u^{*2}f_{iv}^{(4)}+uu^*f_v^{(4)}+f_{vi}^{(4)})$

$F_2^{(4)}=-\frac{\alpha_3^2(\alpha_1+\alpha_2)}{12}[(p+1)(p+2)]^{1/2}u^2f_i^{(4)}$

$f_i^{(4)}=\frac{111}{2}+37\kappa+\frac{19}{2}\kappa^2+\kappa^3$

$f_{ii}^{(4)}=\frac{993}{16}+\frac{331}{8}\kappa+\frac{79}{8}\kappa^2+\kappa^3$

$f_{iii}^{(4)}=\frac{529}{8}\kappa^2+\frac{33}{4}\kappa^3+\frac{1}{2}\kappa^4$

$f_{iv}^{(4)}=5+4\kappa+\kappa^2$

$f_v^{(4)}=\frac{579}{10}+\frac{193}{5}\kappa+\frac{67}{5}\kappa^2+\frac{14}{5}\kappa^3$

$f_{vi}^{(4)}=\frac{337}{5}\kappa^2+\frac{48}{5}\kappa^3+\frac{7}{5}\kappa^4$

tric field perturbation is proportional to $\hat{z}$ and because the zeroth-order function is an eigenfunction of $\hat{z}$ inversion (Bethe and Salpeter, 1957). Although odd powers of $E_{||}$ and half-integral powers of γ disappear for different reasons, the two phenomena are related. This is indicated by the facts that, in Table III, $\mathscr{E}^{(3)}=\mathscr{E}^{(3,0)}$ is proportional to $\mathscr{E}^{(0,2)}$ and the $\alpha_3^4(p+\frac{1}{2})^2$ term in $\mathscr{E}^{(6)}=\mathscr{E}^{(6,0)}$ is proportional to $\mathscr{E}^{(0,4)}$.

The lowest-order cross term in the fields is $\mathscr{E}^{(2,2)}$, which agrees with the result given by Lambin, Van Hay, and Kartheuser (1978) for the one-body problem. The coupling between the CM and internal coordinates does not affect cross terms in the energy until higher order in γ.

We now examine the energy expansion in the infinite-nuclear-mass limit, $\delta=m_1/m_2\to 0$. The coefficients α_1–α_4 in Eqs. (5.60)–(5.63) then reduce to

$$\alpha_1=0\,, \tag{5.88}$$

$$\alpha_2=\tfrac{1}{2}\,, \tag{5.89}$$

$$\alpha_3=0\,, \tag{5.90}$$

$$\alpha_4=1\,. \tag{5.91}$$

TABLE II. Polynomials $G^{(i/2)}$ through $i=8$, as defined in Eq. (5.84). The functions $f^{(5/2)}$, $f_{\rm i}^{(3)}$, etc., are as given in Table I.

$$G^{(0)} = W^{*p}$$

$$G^{(3/2)} = \alpha_3(pW^{*p-1}u^* + W^{*p+1}u)\left[1+\frac{\kappa}{2}\right]$$

$$G^{(2)} = -\frac{\alpha_3}{24}W^{*p}[uu^*(\tfrac{3}{2}+\kappa)+\kappa^2]$$

$$G^{(5/2)} = \frac{\alpha_3(\alpha_1+\alpha_2)}{6}(pW^{*p-1}u^* - W^{*p+1}u)f^{(5/2)}$$

$$G^{(3)} = \frac{\alpha_3^2}{8}\{[p(p-1)W^{*p-2}u^{*2}+W^{*p+2}u^2]f_{\rm i}^{(3)}+(2p+1)W^{*p}(uu^*f_{\rm i}^{(3)}+f_{\rm ii}^{(3)})\}$$

$$G^{(7/2)} = \frac{\alpha_3}{24}(pW^{*p-1}u^* + W^{*p+1}u)\left[(\alpha_1+\alpha_2)^2 f_{\rm i}^{(7/2)} - \frac{\alpha_4}{2}(uu^*f_{\rm ii}^{(7/2)}+f_{\rm iii}^{(7/2)})\right]$$

$$G^{(4)} = \frac{\alpha_3^2(\alpha_1+\alpha_2)}{12}[p(p-1)W^{*p-2}u^{*2} - W^{*p+2}u^2]f_{\rm i}^{(4)} - \frac{\alpha_3^2(\alpha_1+\alpha_2)}{30}W^{*p}(uu^*f_{\rm ii}^{(4)}+f_{\rm iii}^{(4)}) + \frac{\alpha_4^2}{1152}W^{*p}(u^2u^{*2}f_{\rm iv}^{(4)}+uu^*f_{\rm v}^{(4)}+f_{\rm vi}^{(4)})$$

The corresponding energy coefficients in the last column of Table III have no dependence whatsoever upon p, with all of the odd-order terms vanishing identically (Galindo and Pascual, 1976).

Furthermore, the atomic units are defined in terms of μ, which goes to m_1 in the limit that $m_2\to\infty$. Therefore, Eqs. (5.52)—(5.54) become

$$a_\infty = \frac{\hbar^2}{m_1 Z q^2} = \frac{a_0}{1+\delta}\ , \tag{5.92}$$

$$\mathscr{E}_\infty = \frac{\hbar^2}{m_1 a_\infty^2} = \frac{m_1 Z^2 q^4}{\hbar^2} = \mathscr{E}_0(1+\delta)\ , \tag{5.93}$$

$$B_\infty = \frac{\hbar c}{q a_\infty^2} = \frac{m_1^2 Z^2 q^3 c}{\hbar^3} = B_0(1+\delta)^2\ , \tag{5.94}$$

and $\gamma=\underline{B}/B_0$ reduces to

$$\underline{\gamma}_\infty = \frac{\underline{B}}{B_\infty} = \frac{\underline{\gamma}}{(1+\delta)^2}\ . \tag{5.95}$$

The Hamiltonian $\mathscr{H}_U$ can be seen from Appendix B to have the limiting form

$$\mathscr{H}_{U\infty} = -\tfrac{1}{2}\nabla_\kappa^2 - \frac{i}{2}\underline{\gamma}_\infty\cdot\underline{\kappa}\times\nabla_\kappa + \tfrac{1}{8}(\underline{\gamma}_\infty\times\underline{\kappa})^2 - \frac{1}{\kappa}\ , \tag{5.96}$$

where all CM dependence has dropped out and the atomic units are defined by

$$m_1 = \hbar = a_\infty = 1 \tag{5.97}$$

instead of by Eq. (5.51). Thus the eigenvalue of $\mathscr{H}_{U\infty}$ is

$$\mathscr{E}' = \mathscr{E}_\infty\sum_{i=0}^{\infty}\gamma_\infty^{2i}\mathscr{E}^{(2i)}(\delta=0) = \mathscr{E}_0\sum_{i=0}^{\infty}\gamma^{2i}(1+\delta)^{1-2i}\mathscr{E}^{(2i)}(\delta=0)\ , \tag{5.98}$$

where we have explicitly accounted for the vanishing of the coefficients of odd order. It is seen that $\mathscr{E}'$ differs from $\mathscr{E}$ by the unit of energy, the expansion parameter, and the form of the energy coefficients.

TABLE III. Energy coefficients for $n=1$ through order γ^6. All half-integral-order contributions $\mathscr{E}^{[(2k+1)/2]}$ vanish. The constants α_1—α_4 are defined in Eqs. (5.60)—(5.63). Also presented are the results obtained in the infinite-nuclear-mass limit $\delta=m_1/m_2=0$.

k	$\mathscr{E}^{(k)}$	$\mathscr{E}^{(k)}(\delta=0)$
0	$-\frac{1}{2}$	$-\frac{1}{2}$
1	$\alpha_1(p+\frac{1}{2})$	0
2	$\frac{\alpha_4}{4}$	$\frac{1}{4}$
3	$-9\alpha_3^2(p+\frac{1}{2})$	0
4	$\frac{43}{4}\alpha_3^2(\alpha_1+\alpha_2)-\frac{53}{192}\alpha_4^2$	$-\frac{53}{192}$
5	$[\frac{93}{2}\alpha_4-\frac{319}{6}(\alpha_1+\alpha_2)^2]\alpha_3^2(p+\frac{1}{2})$	0
6	$\frac{5581}{4608}\alpha_4^3+\frac{9673}{144}\alpha_3^2(\alpha_1+\alpha_2)^3-\frac{8989}{96}\alpha_3^2\alpha_4(\alpha_1+\alpha_2)-\frac{8541}{32}\alpha_3^4-\frac{3555}{4}\alpha_3^4(p+\frac{1}{2})^2$	$\frac{5581}{4608}$

We have gone into detail here to make clear that our results, based upon conversion to CM and internal coordinates followed by the PZW transformation, coincide in the infinite-mass limit with those of the usual one-body calculations based upon $H_{\rm mc}$ in Eq. (3.3) with $E=0$. Taking $\delta\to 0$ with m_1 fixed, this is

$$H'=\lim_{\delta\to 0}H_{\rm mc}=\frac{1}{2m_1}\left[\underline{p}_1-\frac{e_1}{2c}\underline{B}\times\underline{r}_1\right]^2+\frac{e_1e_2}{|\underline{r}_1-\underline{r}_2|}$$
$$=\frac{p_1^2}{2m_1}+\frac{q}{2m_1c}\underline{B}\cdot\underline{r}_1\times\underline{p}_1+\frac{q^2}{8m_1c^2}(\underline{B}\times\underline{r})^2-\frac{Zq^2}{r_1}$$
$$=-\tfrac{1}{2}\nabla_{r_1}^2-\frac{i}{2}\underline{\gamma}_\infty\cdot\underline{r}_1\times\nabla_{r_1}+\tfrac{1}{8}(\underline{\gamma}_\infty\times\underline{r}_1)^2-\frac{1}{r_1}\ . \tag{5.99}$$

In the second line $\underline{r}_2$ has been taken to be the origin, and in the third line the infinite-mass atomic units of Eq. (5.97) have been adopted. Thus H' has the same form as $\mathscr{H}_{U\infty}$ and leads to the same energy $\mathscr{E}'$.

Actually, it is not necessary to compare the energy $\mathscr{E}$ with the results $\mathscr{E}'$ obtained in the literal infinite-mass limit. This is because the standard *field-free* prescription for making finite-nuclear-mass corrections, replacing m_1 by μ in the one-body Hamiltonian, can be made. Such a modification corresponds to using, instead of H', the (somewhat *ad hoc*) Hamiltonian

$$H''=\frac{p_1^2}{2\mu}+\frac{q}{2\mu c}\underline{B}\cdot\underline{r}_1\times\underline{p}_1+\frac{q^2}{8\mu c^2}(\underline{B}\times\underline{r}_1)^2-\frac{Zq^2}{r_1}$$
$$=-\tfrac{1}{2}\nabla_{r_1}^2-\frac{i}{2}\underline{\gamma}\cdot\underline{r}_1\times\nabla_{r_1}+\tfrac{1}{8}(\underline{\gamma}\times\underline{r}_1)^2-\frac{1}{r_1}\ , \tag{5.100}$$

where the reduced units of Eq. (5.51) have been employed in the last line. It is clear that H'' leads to the perturbation expansion

$$\mathscr{E}''=\mathscr{E}_0\sum_{i=0}^{\infty}\gamma^{2i}\mathscr{E}^{(2i)}(\delta=0)\ , \tag{5.101}$$

in which the errors engendered by use of the infinite-mass atomic units have been corrected. Thus the results of one-body calculations can be simply adjusted so that it is necessary for us to compare only the energy coefficients $\mathscr{E}^{(i)}$ for $\delta\neq 0$ and for $\delta=0$.

Some representative numbers are given in Table IV for $Z=2$ and for three different values of the mass ratio: (i) $\delta=0$, corresponding to the infinite-nuclear-mass limit, (ii) $\delta=1.3606\times10^{-4}$, appropriate to the $^4He^+$ ion, with the masses taken from the tables of Cohen and Taylor (1973), and (iii) $\delta=1$, representing a hypothetical two-body system with equal masses.

The case $\delta=1$ cannot be approximately solved by use of a one-body treatment, as should be evident from a comparison of the $\delta=0$ and $\delta=1$ columns. The coefficients of $p+\frac{1}{2}$ in $\mathscr{E}^{(1)}$, $\mathscr{E}^{(3)}$, and $\mathscr{E}^{(5)}$ are all of about the same order of magnitude as the p-independent terms for $\delta=1$. In contrast to this, the p-dependent terms for the helium ion have quite small coefficients because of the small electronic-to-nuclear mass ratio. The *separation of adjacent levels* in $^4He^+$ is well approximated by the difference in first-order energies, $\Delta\mathscr{E}(\text{eV})\cong\mathscr{E}_0\alpha_1\gamma\simeq 8\times10^{-11}$ B(G), which is of the same order of magnitude as the magnetic hyperfine splitting.

The one-body treatment is powerless to obtain such terms, but we see that the dominant p-independent contributions in helium are obtained accurately within the number of significant figures retained. *The fractional differences in the even-order energy coefficients* (or, equivalently, hypersusceptibilities) can be obtained from Table III. If we define

$$\Delta^{(2i)}=\frac{\mathscr{E}^{(2i)}(\delta=1.3606\times10^{-4})-\mathscr{E}^{(2i)}(\delta=0)}{\mathscr{E}^{(2i)}(\delta=0)}\ , \tag{5.102}$$

then

TABLE IV. Numerical results of parameters and energy coefficients for $n=1$ for three different values of the mass ratio δ. The value $\delta=1.3606\times10^{-4}$ corresponds to $^4He^+$.

	$\delta=0$	$\delta=1.3606\times10^{-4}$	$\delta=1$
α_1	0.0000	1.3602×10^{-4}	2.5000×10^{-1}
α_2	5.0000×10^{-1}	4.9986×10^{-1}	-1.2500×10^{-1}
α_3	0.0000	9.6196×10^{-5}	2.6517×10^{-1}
α_4	1.0000	1.0000	2.3125
$\mathscr{E}^{(0)}$	-5.0000×10^{-1}	-5.0000×10^{-1}	-5.0000×10^{-1}
$\mathscr{E}^{(1)}$	0.0000	$1.3602\times10^{-4}(p+\frac{1}{2})$	$2.5000\times10^{-1}(p+\frac{1}{2})$
$\mathscr{E}^{(2)}$	2.5000×10^{-1}	2.5000×10^{-1}	5.7812×10^{-1}
$\mathscr{E}^{(3)}$	0.0000	$-8.3283\times10^{-4}(p+\frac{1}{2})$	$-6.3284\times10^{-1}(p+\frac{1}{2})$
$\mathscr{E}^{(4)}$	-2.7604×10^{-1}	-2.7604×10^{-1}	-1.3817
$\mathscr{E}^{(5)}$	0.0000	$3.0730\times10^{-7}(p+\frac{1}{2})$	$7.5027(p+\frac{1}{2})$
$\mathscr{E}^{(6)}$	1.2112	1.2112	1.1764×10^{1}
		$-7.6104\times10^{-14}(p+\frac{1}{2})^2$	$-4.3942(p+\frac{1}{2})^2$

$$\Delta^{(2)}=\alpha_4-1\cong 1.11\times 10^{-7}\,, \tag{5.103}$$

$$\Delta^{(4)}\cong 4.19\times 10^{-8}\,, \tag{5.104}$$

$$\Delta^{(6)}\cong 3.94\times 10^{-8}-6.28\times 10^{-14}(p+\tfrac{1}{2})^2\,. \tag{5.105}$$

Thus the errors in even order are beyond concern for anything except fantastically precise measurements [in which case relativistic effects should also be taken into account—see Grotch and Hegstrom (1971)]. The most important term by far, $\mathscr{E}^{(2)}$, is obtained to about one part in 10^7 by use of the one-body Hamiltonian H'' in which the a_0/a_∞, $\mathscr{E}_0/\mathscr{E}_\infty$, and B_0/B_∞ differences have been taken into account. [Of course, the literal infinite-mass results contained in Eq. (5.98) compare less favorably.] We also see that the sixth-order error $\Delta^{(6)}$ is dominated by the $(p+\frac{1}{2})^2$ term only for $p\gtrsim 10^3$.

We note that, although the procedures we have followed explicitly assume that $Z\neq 1$, the perturbed energies reduce in the limit $Z\to 1$ to those for $K_\perp=0$ in the neutral problem of Sec. IV.

D. Excited states ($n=2$)

For $n=2$, there are in general four functions $\psi_\nu(\underline{\kappa},W,W^*)$, with $\nu=a,b,c$, and d, for which the operator $\mathscr{L}_1$ has a given eigenvalue p. These functions may be represented as in Eq. (5.68) by column vectors $\underline{\chi}_\nu$ composed of internal functions $\chi_{\nu m}$,

$$\underline{\chi}_\nu=\sum_{m=-p}^{\infty}\underline{e}_{m+p}\chi_{\nu m}\,. \tag{5.106}$$

The vectors $\underline{\chi}_\nu$ must satisfy

$$(\underline{\underline{h}}-\mathscr{E}_\nu\underline{\underline{1}})\underline{\chi}_\nu=0\,, \tag{5.107}$$

$$\langle\underline{\chi}_{\nu'}\,|\,\underline{\chi}_\nu\rangle=0\quad(\nu\neq\nu')\,, \tag{5.108}$$

where the matrix operator $\underline{\underline{h}}$ is given in expanded form in Eq. (5.55).

If the $\underline{\chi}_\nu$ are expanded in powers of $\gamma^{1/2}$, then in zeroth order the $\underline{\chi}^{(0)}_{\nu m}$ are given by the $\Phi_{2lm}(\underline{\kappa})$ of Eq. (4.67),

$$\underline{\chi}^{(0)}_a=\underline{e}_{p-1}\chi^{(0)}_{a-1}=\underline{e}_{p-1}\Phi_{21-1}\,, \tag{5.109}$$

$$\underline{\chi}^{(0)}_b=\underline{e}_p\chi^{(0)}_{b0}=\underline{e}_p\Phi_{200}\,, \tag{5.110}$$

$$\underline{\chi}^{(0)}_c=\underline{e}_{p+1}\chi^{(0)}_{c1}=\underline{e}_{p+1}\Phi_{211}\,, \tag{5.111}$$

$$\underline{\chi}^{(0)}_d=\underline{e}_p\chi^{(0)}_{d0}=\underline{e}_p\Phi_{210}\,, \tag{5.112}$$

and the corresponding $\psi^{(0)}_\nu$ are then

$$\psi^{(0)}_a=\psi_{\perp;p-1}\Phi_{21-1}\,, \tag{5.113}$$

$$\psi^{(0)}_b=\psi_{\perp;p}\Phi_{200}\,, \tag{5.114}$$

$$\psi^{(0)}_c=\psi_{\perp;p+1}\Phi_{211}\,, \tag{5.115}$$

$$\psi^{(0)}_d=\psi_{\perp;p}\Phi_{210}\,, \tag{5.116}$$

with $\psi_{\perp;n_1}(W,W^*)$ defined in Eq. (5.43). The four states are degenerate in this order with $\mathscr{E}^{(0)}_\nu=\mathscr{E}^{(0)}=-\frac{1}{8}$.

The wave function $\psi^{(0)}_d$ is the only one which is odd under inversion of $\check{z}$, and consequently the perturbation calculations proceed as in the nondegenerate case. The perturbed component wave functions have the form

$$\chi^{(i/2)}_{dm}=\frac{1}{4(2\pi)^{1/2}}F^{(i/2)}_{dm}(\underline{\kappa})e^{-\kappa/2}\,, \tag{5.117}$$

where $F^{(i/2)}_{dm}$ is a polynomial in κ, u, and u^* times an overall factor of $\check{z}$. These polynomials are again calculated by making the similarity transformation $\exp(\kappa/2)$ and solving the resulting inhomogeneous equations through use of the relation

$$\begin{aligned}\bar{\eta}^{(0)}_2\kappa^j u^k u^{*l}\check{z}=&\frac{j+k+l}{2}\kappa^{j-1}u^k u^{*l}\check{z}\\&-\frac{j(j+3+2k+2l)}{2}\kappa^{j-2}u^k u^{*l}\check{z}\\&-2kl\kappa^j u^{k-1}u^{*l-1}\check{z}\,,\end{aligned} \tag{5.118}$$

where [cf. Eq. (4.60)]

$$\bar{\eta}^{(0)}_2=e^{\kappa/2}(h^{(0)}-\mathscr{E}^{(0)})e^{-\kappa/2}\,. \tag{5.119}$$

In Table V we list the polynomials through order γ^2 and the energy coefficients through order γ^4. They are similar to the results for $n=1$. In particular, all half-integral-order energy coefficients vanish and α_3 enters into the energy only in the form α_3^2.

A different situation occurs for states a, b, and c. The perturbation calculations turn out to be coupled by the CM-internal coupling terms. This first shows up in order $\gamma^{3/2}$, where we find that $\langle\underline{\chi}^{(0)}_a\,|\,\underline{\underline{h}}^{(3/2)}\,|\,\underline{\chi}^{(0)}_b\rangle$ and $\langle\underline{\chi}^{(0)}_b\,|\,\underline{\underline{h}}^{(3/2)}\,|\,\underline{\chi}^{(0)}_c\rangle$ do not vanish. This is due to the extra degeneracy and the fact that u and u^* matrix elements between the zeroth-order internal functions do not all vanish. In order to obtain the perturbed wave functions and energies for the a-b-c manifold, it is necessary to resort to the methods of almost degenerate perturbation theory (Hirschfelder, 1978) which we now briefly describe in the current notation.

Instead of the $\underline{\chi}_\nu$, we shall work with an alternative set of vectors $\underline{\tilde{\chi}}_\rho$, defined by

$$\underline{\chi}_\nu=\sum_\rho\underline{\tilde{\chi}}_\rho C_{\rho\nu}\,, \tag{5.120}$$

TABLE V. Nonvanishing $F^{(i/2)}_{dm}$ through γ^2 and $\mathscr{E}^{(i/2)}_d$ through γ^4. The polynomials $F^{(i/2)}_{dm}$ are defined by Eq. (5.117).

$F^{(0)}_{d0}$	$=\check{z}$
$F^{(3/2)}_{d-1}$	$=\alpha_3(p)^{1/2}(6+\kappa)u^*\check{z}$
$F^{(3/2)}_{d1}$	$=\alpha_3(p+1)^{1/2}(6+\kappa)u\check{z}$
$F^{(2)}_{d0}$	$=-\frac{\alpha_4}{12}[(4+\kappa)uu^*+2\kappa^2]\check{z}$
$\mathscr{E}^{(0)}_d$	$=-\frac{1}{8}$
$\mathscr{E}^{(1)}_d$	$=\alpha_1(p+\frac{1}{2})$
$\mathscr{E}^{(2)}_d$	$=\frac{3}{2}\alpha_4$
$\mathscr{E}^{(3)}_d$	$=-312\alpha_3^2(p+\frac{1}{2})$
$\mathscr{E}^{(4)}_d$	$=2112\alpha_3^2(\alpha_1+\alpha_2)-42\alpha_4^2$

where both ν and ρ run over a, b, and c, and $\underline{\underline{C}}$ is a nonsingular 3×3 matrix. Using Eqs. (5.107) and (5.120), we can easily show that the $\underline{\tilde{\chi}}_\rho$ satisfy the coupled equations

$$\underline{\underline{h}}\underline{\tilde{\chi}}_\rho=\sum_{\rho'}\underline{\tilde{\chi}}_{\rho'}\tilde{\mathscr{E}}_{\rho'\rho}\ , \tag{5.121}$$

where

$$\tilde{\mathscr{E}}_{\rho'\rho}=\sum_{\nu}C_{\rho'\nu}\mathscr{E}_\nu C^{-1}_{\nu\rho}\ . \tag{5.122}$$

Expansion of $\underline{\tilde{\chi}}_\rho$ and $\tilde{\mathscr{E}}_{\rho'\rho}$ in powers of $\gamma^{1/2}$,

$$\underline{\tilde{\chi}}_\rho=\sum_{i=0}^{\infty}\gamma^{i/2}\underline{\tilde{\chi}}_\rho^{(i/2)}\ , \tag{5.123}$$

$$\tilde{\mathscr{E}}_{\rho'\rho}=\sum_{i=0}^{\infty}\gamma^{i/2}\tilde{\mathscr{E}}_{\rho'\rho}^{(i/2)}\ , \tag{5.124}$$

then leads to the perturbation equations

$$\sum_{i=0}^{k}\left[\underline{\underline{h}}^{(i/2)}\underline{\tilde{\chi}}_\rho^{[(k-i)/2]}-\sum_{\rho'}\underline{\tilde{\chi}}_{\rho'}^{[(k-i)/2]}\tilde{\mathscr{E}}_{\rho'\rho}^{(i/2)}\right]=0\ . \tag{5.125}$$

The zeroth-order equation is satisfied by equating the $\underline{\tilde{\chi}}_\rho^{(0)}$ to the $\underline{\chi}_\nu^{(0)}$ in Eqs. (5.109)–(5.111), and the energy matrix is obviously diagonal in this order:

$$\tilde{\mathscr{E}}_{\rho'\rho}^{(0)}=-\tfrac{1}{8}\delta_{\rho'\rho}\ . \tag{5.126}$$

Multiplication of Eq. (5.125) by $(\underline{\tilde{\chi}}_{\rho''}^{(0)})^\dagger$ and integration then yields the equation

$$\begin{aligned}\tilde{\mathscr{E}}_{\rho''\rho}^{(k/2)}=&\langle\underline{\tilde{\chi}}_{\rho''}^{(0)}|\underline{\underline{h}}^{(k/2)}|\underline{\tilde{\chi}}_\rho^{(0)}\rangle\\&+\sum_{i=1}^{k-1}\left[\langle\underline{\tilde{\chi}}_{\rho''}^{(0)}|\underline{\underline{h}}^{(i/2)}|\underline{\tilde{\chi}}_\rho^{[(k-i)/2]}\rangle\right.\\&\left.-\sum_{\rho'}\langle\underline{\tilde{\chi}}_{\rho''}^{(0)}|\underline{\tilde{\chi}}_{\rho'}^{[(k-i)/2]}\rangle\tilde{\mathscr{E}}_{\rho'\rho}^{(i/2)}\right]\ ,\end{aligned} \tag{5.127}$$

in which the $i=0$ term has dropped out, as usual, by the hermiticity of $h^{(0)}$ and use has been made of the orthonormality of the $\tilde{\chi}_\rho^{(0)}$. Thus $\tilde{\mathscr{E}}_{\rho''\rho}^{(k/2)}$ can be obtained from knowledge of all $\tilde{\mathscr{E}}_{\rho'\rho}^{(i/2)}$ and $\underline{\tilde{\chi}}_\rho^{(i/2)}$ for $i<k$. The remaining unknowns in Eqs. (5.125) are then the $\underline{\tilde{\chi}}_\rho^{(k/2)}$. These functions are, again, simply polynomials times $\exp(-\kappa/2)$,

$$\tilde{\chi}_{\rho m}^{(k/2)}=N_\rho\tilde{F}_{\rho m}^{(k/2)}(\kappa)e^{-\kappa/2}\ , \tag{5.128}$$

where

$$\begin{aligned}N_a&=N_c=\tfrac{1}{8}\pi^{-1/2}\ ,\\N_b&=\tfrac{1}{4}(2\pi)^{-1/2}\ ,\end{aligned} \tag{5.129}$$

and can be calculated with the aid of the relation

$$\begin{aligned}\bar{\eta}_2^{(0)}\kappa^j u^k u^{*l}=&\frac{j+k+l-1}{2}\kappa^{j-1}u^k u^{*l}\\&-\frac{j(j+1+2k+2l)}{2}\kappa^{j-2}u^k u^{*l}\\&-2kl\kappa^j u^{k-1}u^{*l-1}\ .\end{aligned} \tag{5.130}$$

The polynomials $\tilde{F}_{\rho m}^{(i/2)}$ through $i=4$ are tabulated in Table VI.

TABLE VI. Nonvanishing $\tilde{F}_{\rho m}^{(i/2)}$ through $i=4$ for $\rho=a$, b, and c. The polynomials $\tilde{F}_{\rho m}^{(i/2)}$ are defined in Eq. (5.128).

$\tilde{F}_{a-1}^{(0)}$	$=u^*$
$\tilde{F}_{a-2}^{(3/2)}$	$=\alpha_3(p-1)^{1/2}u^{*2}(6+\kappa)$
$\tilde{F}_{a0}^{(3/2)}$	$=\alpha_3 p^{1/2}[uu^*(6+\kappa)-8\kappa^2]$
$\tilde{F}_{a-1}^{(2)}$	$=-\frac{\alpha_4}{12}u^*[uu^*(4+\kappa)+4\kappa^2]$
$\tilde{F}_{b0}^{(0)}$	$=2-\kappa$
$\tilde{F}_{b-1}^{(3/2)}$	$=-\alpha_3 p^{1/2}u^*\kappa^2$
$\tilde{F}_{b1}^{(3/2)}$	$=-\alpha_3(p+1)^{1/2}u\kappa^2$
$\tilde{F}_{b0}^{(2)}$	$=\frac{\alpha_4}{12}[uu^*(24+4\kappa+\kappa^2)-44\kappa^2+2\kappa^3]$
$\tilde{F}_{c1}^{(0)}$	$=-u$
$\tilde{F}_{c0}^{(3/2)}$	$=-\alpha_3(p+1)^{1/2}[uu^*(6+\kappa)-8\kappa^2]$
$\tilde{F}_{c2}^{(3/2)}$	$=-\alpha_3(p+2)^{1/2}u^2(6+\kappa)$
$\tilde{F}_{c1}^{(2)}$	$=\frac{\alpha_4}{12}u[uu^*(4+\kappa)+\kappa^2]$

Through the same order, the complete 3×3 energy matrix is

$$\underline{\underline{\tilde{\mathscr{E}}}}=\begin{bmatrix}-\frac{1}{8}+\alpha_1(p-\frac{1}{2})\gamma-\alpha_2\gamma+3\alpha_4\gamma^2 & 3(2p)^{1/2}\alpha_3\gamma^{3/2} & 0\\ 3(2p)^{1/2}\alpha_3\gamma^{3/2} & -\frac{1}{8}+\alpha_1(p+\frac{1}{2})\gamma+\frac{7}{2}\alpha_4\gamma^2 & -3[2(p+1)]^{1/2}\alpha_3\gamma^{3/2}\\ 0 & -3[2(p+1)]^{1/2}\alpha_3\gamma^{3/2} & -\frac{1}{8}+\alpha_1(p+\frac{3}{2})\gamma+\alpha_2\gamma+3\alpha_4\gamma^2\end{bmatrix}\ . \tag{5.131}$$

Although this matrix is Hermitian, careful specification of the normalization conditions for the perturbed wave functions would be required to ensure this in higher order.

Whereas α_3 did not contribute to the energy until order γ^3 in the earlier cases, it now appears in the off-diagonal elements at order $\gamma^{3/2}$. This, as stated before, is due to the extra degeneracy. The relevant question is, of course, the form of the eigenvalues $\mathscr{E}_\nu$. In order to obtain these for general p, it is necessary to solve the secular equation resulting from the full 3×3 matrix $\tilde{\mathscr{E}}$. We shall not do this, but point out the readily verified fact that the secular equation depends only upon α_3^2, not α_3.

There are two simple cases, $p=-1$ and $p=0$, which we discuss briefly. For $p=-1$, examination of Eqs. (5.113)—(5.116) shows that, instead of four states, there is only the state emanating from

$$\psi_c^{(0)}=\psi_{\perp;0}\Phi_{211}\ . \tag{5.132}$$

The states a, b, and d are eliminated because the corresponding magnetic field wave functions $\psi_{\perp;n_1}$ would be characterized by negative n_1. Therefore, the calculations will proceed as in the nondegenerate (uncoupled) case. The resulting wave function and energy correct through γ^2 are the same as in Table VI and the (c,c) element of Eq. (5.131), respectively, with p set equal to -1.

For $p=0$, there are three states possible. These originate from

$$\begin{aligned}\psi_b^{(0)}&=\psi_{\perp;0}\Phi_{200}\ ,\\ \psi_c^{(0)}&=\psi_{\perp;1}\Phi_{211}\ ,\\ \psi_d^{(0)}&=\psi_{\perp;0}\Phi_{210}\ .\end{aligned} \tag{5.133}$$

Only b and c are coupled, and their energy matrix is obtained from the lower right 2×2 block of Eq. (5.131) with $p=0$,

$$\begin{bmatrix}\tilde{\mathscr{E}}_{bb} & \tilde{\mathscr{E}}_{bc}\\ \tilde{\mathscr{E}}_{cb} & \tilde{\mathscr{E}}_{cc}\end{bmatrix}=\begin{bmatrix}-\frac{1}{8}+(\alpha_1\gamma/2)+\frac{7}{2}\alpha_4\gamma^2 & -3\sqrt{2}\alpha_3\gamma^{3/2}\\ -3\sqrt{2}\alpha_3\gamma^{3/2} & -\frac{1}{8}+\frac{3}{2}\alpha_1\gamma+\alpha_2\gamma+3\alpha_4\gamma^2\end{bmatrix}. \tag{5.134}$$

The exact eigenvalues of this matrix are

$$\begin{aligned}\mathscr{E}_b&=-\frac{1}{8}+\left[\alpha_1+\frac{\alpha_2}{2}\right]\gamma+\tfrac{13}{4}\alpha_4\gamma^2-\frac{\gamma}{2}\left[\left[\alpha_1+\alpha_2-\frac{\alpha_4\gamma}{2}\right]^2+72\alpha_3^2\gamma\right]^{1/2},\\ \mathscr{E}_c&=-\frac{1}{8}+\left[\alpha_1+\frac{\alpha_2}{2}\right]\gamma+\tfrac{13}{4}\alpha_4\gamma^2+\frac{\gamma}{2}\left[\left[\alpha_1+\alpha_2-\frac{\alpha_4\gamma}{2}\right]^2+72\alpha_3^2\gamma\right]^{1/2}.\end{aligned} \tag{5.135}$$

However, the calculation is valid only through γ^2. Accordingly, we expand the square root in powers of γ to obtain

$$\begin{aligned}\mathscr{E}_b&\cong-\frac{1}{8}+\frac{\alpha_1}{2}\gamma+\tfrac{7}{2}\alpha_4\gamma^2-\frac{18\alpha_3^2}{\alpha_1+\alpha_2}\gamma^2\ ,\\ \mathscr{E}_c&\cong-\frac{1}{8}+\tfrac{3}{2}\alpha_1\gamma+\alpha_2\gamma+3\alpha_4\gamma^2+\frac{18\alpha_3^2}{\alpha_1+\alpha_2}\gamma^2\ .\end{aligned} \tag{5.136}$$

Thus we have the interesting result that the coupling due to the extra degeneracy makes contributions to the energy at order γ^2. Inspection of Table IV shows that, for $^4He^+$, the coefficients of γ^2 in the last terms are extremely small,

$$\frac{18\alpha_3^2}{\alpha_1+\alpha_2}\cong3.33\times10^{-7}\ . \tag{5.137}$$

This is of the same order of magnitude as α_4-1 in Eq. (5.103), and we conclude that the diamagnetic susceptibility is still extremely well approximated by the usual one-body results. This is obviously not true for the hypothetical example of equal masses, however.

The remark at the end of Sec. IV.D about symmetric top molecules with permanent dipole moments also has its analog here. Just as for the excited states of the hydrogenic ion, the nonvanishing of the dipole moment expectation value in zeroth order leads to coupling in the perturbation calculations. In practice, this coupling is so weak that it may safely be ignored.

We have demonstrated that the perturbed wave functions and energies for an ionic two-body system can be calculated to arbitrary order using only bound-state techniques. [Note that simply expanding $\mathscr{H}_U$ of Eq. (5.22) in powers of the magnetic field gives a zeroth-order Hamiltonian in which the CM motion is that of a free particle.] For small values of the mass ratio δ, as are usually encountered, it is evident that one will not want to take into account the CM-internal coupling. From the numerical results presented here, we see that it is normally justifiable to ignore $\underline{\underline{h}}^{(3/2)}$, which may be done by setting $\alpha_3=0$, leaving all other quantities alone. This reduces Eq. (5.55) to diagonal form, and the perturbation calculation to the usual one-body problem (except for the small differences in using the coefficients α_2 and α_4). The resulting internal wave function, when multiplied by $\psi_{\perp;n_1}(W,W^*)$, yields a simultaneous eigenfunction of $\mathscr{H}_s$ and (approximately) of $\mathscr{H}_r$. Afterwards, if it is desired to examine the coupling corrections, this can be done by considering the coupling matrix to be a second perturbation (with parameter $\alpha_3\gamma^{3/2}$), and the already calculated perturbed wave functions can be used as input to the new calculations.

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APPENDIX A: CHARGED SYSTEMS ENTERING A MAGNETIC FIELD

In Sec. II.B, it was shown that the classical values of $\mathcal{X}_x$ and $\mathcal{X}_y$ are integration constants. These may be fixed by imposing initial conditions upon the trajectory. One example of this, for which we shall give the quantum analog, is the deflection of a charged particle entering a region which contains a constant magnetic field. Figure 4 describes the trajectory of the particle as it enters from the field-free half-plane (region I) into the field (region II) at time $t=0$. The initial velocity is $\underline{v}_i=(v_{ix},v_{iy},0)$, and the final velocity $\underline{v}_f=(-v_{ix},v_{iy},0)$. While in the field, the orbit is a portion of that which would be followed if the field were present in the entire plane. This is the basis for the early experimental measurements of the electronic charge-to-mass ratio e/M [at least when the initial y velocity is zero—see Uhlenbeck and Young (1930)].

For $t<0$, we have

$$X=v_{ix}t\ , \tag{A1}$$

$$Y=Y_0+v_{iy}t\quad (t<0)\ , \tag{A2}$$

where Y_0 is the value of Y at the first crossing between regions. From Eqs. (2.15) and (2.17), the general solutions for region II are

$$X=\rho\sin(\omega t+\theta)+X_c\ , \tag{A3}$$

$$Y=\rho\cos(\omega t+\theta)+Y_c\ . \tag{A4}$$

Matching coordinates and velocities at $t=0$ yields

$$\theta=\tan^{-1}(-v_{iy}/v_{ix})\ , \tag{A5}$$

$$\rho=(v_{ix}^2+v_{iy}^2)^{1/2}/\omega=v_i/\omega\ , \tag{A6}$$

$$X_c=-\rho\sin\theta=v_{iy}/\omega\ , \tag{A7}$$

$$Y_c=Y_0-\rho\cos\theta=Y_0-v_{ix}/\omega\ . \tag{A8}$$

Thus Eqs. (A3) and (A4) become, in terms of the initial parameters,

$$X=\frac{v_{iy}}{\omega}(1-\cos\omega t)+\frac{v_{ix}}{\omega}\sin\omega t\ , \tag{A9}$$

$$Y=\frac{v_{iy}}{\omega}\sin\omega t+\frac{v_{ix}}{\omega}(\cos\omega t-1)+Y_0 \qquad (0<t<T)\ . \tag{A10}$$

The return to region I occurs at time $t=T$ for which, from the geometry of the orbit,

$$\omega T=2\left[\frac{\pi}{2}-\theta\right]=2\tan^{-1}(-v_{ix}/v_{iy})\ , \tag{A11}$$

at which point rectilinear motion is regained:

$$X=-v_{ix}(t-T)\ , \tag{A12}$$

$$Y=Y_0-2\frac{v_{ix}}{\omega}+v_{iy}(t-T)\quad (t>T)\ . \tag{A13}$$

A quantum-mechanical description of this event can be obtained by matching energy-dependent wave functions for regions I and II at the boundary line $X=0$. This is a simple generalization of the work of Uhlenbeck and Young, who treated the case where the motion in region I is restricted to be parallel to the x axis. For the general case, the wave function in region I must satisfy

$$\left[\frac{1}{2M}P_1^2-\mathscr{E}\right]\psi_{\rm I}(X,Y)=0\ , \tag{A14}$$

where $\mathscr{E}$ is given by

$$\mathscr{E}=\frac{\hbar^2}{2M}(K_x^2+K_y^2)\ , \tag{A15}$$

and K_x and K_y are related to the initial velocity components by

$$v_{ix}=\hbar K_x/M\ , \tag{A16}$$

$$v_{iy}=\hbar K_y/M\ . \tag{A17}$$

The general solution is therefore

$$\psi_{\rm I}(X,Y)=e^{iK_yY}(ae^{iK_xX}+be^{-iK_xX})\ , \tag{A18}$$

where the first term represents the incoming wave and the second term the outgoing wave. The constants a and b remain to be determined.

In region II, the wave function must obey

$$\left[\frac{1}{2M}\Pi_1^2-\mathscr{E}\right]\psi_{\rm II}(X,Y)=0\ . \tag{A19}$$

In order to have continuous charge and current densities, we must have

$$\psi_{\rm II}(0,Y)=e^{iK_yY}(a+b)\ , \tag{A20}$$

$$[\Pi_x\psi_{\rm II}]_{X=0}=\left[\left[P_x+\frac{M\omega}{2}Y\right]\psi_{\rm II}\right]_{X=0}=\hbar K_xe^{iK_yY}(a-b)\ , \tag{A21}$$

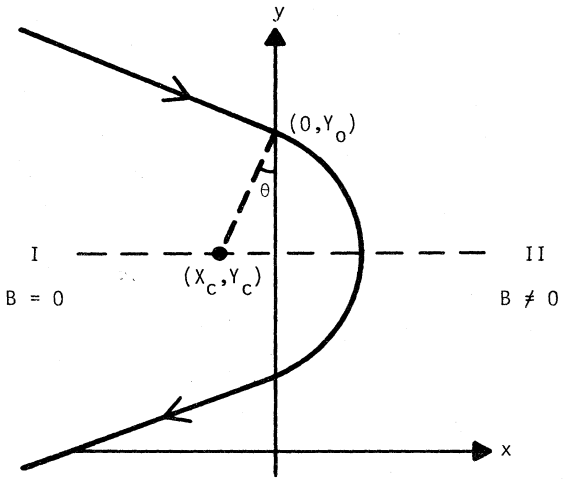

FIG. 4. Deflection of a charged particle entering a magnetic field $\underline{B}=B\hat{z}$.

$$[\Pi_y\psi_{\rm II}]_{X=0}=\left[\left[P_y-\frac{M\omega}{2}X\right]\psi_{\rm II}\right]_{X=0}=\hbar K_y e^{iK_y Y}(a+b)\ . \tag{A22}$$

The remaining boundary condition is that $\psi_{\rm II}$ vanish at $X=+\infty$.

Now the important point to be garnered from the classical discussion is that the coordinate X_c is determined precisely by the incoming momentum $\hbar K_Y$. If we combine Eqs. (A7) and (A17), X_c is given by

$$X_c=\hbar K_y/M\omega\ . \tag{A23}$$

The development in Sec. II.D says that this is accomplished quantum mechanically by making $\psi_{\rm II}$ an eigenfunction of $\mathscr{K}_y^0$ with eigenvalue $\hbar K_y$. The operator $\mathscr{K}_x^0$, which does not commute with $\mathscr{K}_y^0$, is therefore not made sharp; this is consistent with the fact that the plane-wave solution $\psi_{\rm I}$ in Eq. (A18) does not correspond to a definite value of Y_0, the first crossing point [see Eq. (A8)].

Thus the pseudomomentum component

$$\mathscr{K}_y^0=P_y+\frac{M\omega}{2}X \tag{A24}$$

is diagonalized by taking $\psi_{\rm II}$ to have the form

$$\psi_{\rm II}(X,Y)=\exp\left[iK_y Y-\frac{iM\omega}{2\hbar}XY\right]\phi(X)\ , \tag{A25}$$

where $\phi(X)$ obeys the equation

$$\frac{1}{2M}[P_x^2+(\hbar K_y-M\omega X)^2-\hbar^2(K_x^2+K_y^2)]\phi(X)=0\ . \tag{A26}$$

Equations (A20)—(A22) are thereby reduced to the two independent conditions

$$\phi(0)=a+b\ , \tag{A27}$$

$$\left.\frac{d\phi}{dX}\right|_{X=0}=\hbar K_x(a-b)\ , \tag{A28}$$

with, of course, the additional condition that $\phi(\infty)=0$.

The two-dimensional problem is thus essentially one dimensional, and, if the entrance into the field is head-on ($K_y=0$), corresponds to the treatment of Uhlenbeck and Young. If $K_y\neq 0$, the difference is that the origin of the X coordinate has been shifted by $\hbar K_y/M\omega$ in the effective Schrödinger equation (A26).

The point we wish to make is that the eigenvalue of $\mathscr{K}_y^0$ has a definite physical significance in this problem other than its relation to the center of the orbit in a magnetic field (though the two interpretations are related by the classical discussion). In region I, $\mathscr{K}_y^0$ reduces to the mechanical (and canonical) momentum P_y, and $\hbar K_y/M\omega$ can thus be identified as the initial incoming velocity along the y axis.

The example of deflection by a magnetic field is a bit more complicated for charged molecular systems. The claim was made at the end of Sec. V that the CM motion is (to a good approximation) that of a single charged particle, despite the fact that the transverse mechanical momentum,

$$M\dot{\underline{R}}_\perp=\underline{P}_\perp-\frac{e}{2c}\underline{B}\times\underline{R}_\perp-\frac{1}{c}\underline{B}\times\underline{\mu}\ , \tag{A29}$$

has an additional component from the dipole moment. This component should be most significant for a molecule with a permanent dipole moment in the absence of the external field. We can perform a classical calculation which gives some idea of the largest possible order of magnitude of the deviation from the single-particle orbit.

The solid line in Fig. 5 is the orbit of a charged particle which has entered region II with initial velocity along the x axis. (This is the $v_{iy}=0=X_c$ version of Fig. 4.) For further simplicity, we have also chosen $Y_c=0$, so that the single-particle trajectory in region II is, from Eqs. (A9) and (A10),

$$X=\frac{v_i}{\omega}\sin\omega t\ , \tag{A30}$$

$$Y=\frac{v_i}{\omega}\cos\omega t\ . \tag{A31}$$

The time T spent in region II is then one-half of a complete orbital period

$$T=\frac{\pi}{\omega}\ . \tag{A32}$$

Also shown is the perturbed trajectory $\underline{R}_\perp+\delta\underline{R}_\perp$ (dashed line) due to a hypothetical permanent dipole moment additionally interacting with the field

$$M\delta\ddot{\underline{R}}_\perp\cong-\frac{1}{c}\underline{B}\times\dot{\underline{\mu}}\ , \tag{A33}$$

$$\delta\dot{\underline{R}}_\perp\cong-\frac{1}{Mc}\underline{B}\times\underline{\mu}\ . \tag{A34}$$

The magnitude of $\underline{\mu}$ is presumed constant, and the orientation is constrained to give the greatest possible radial

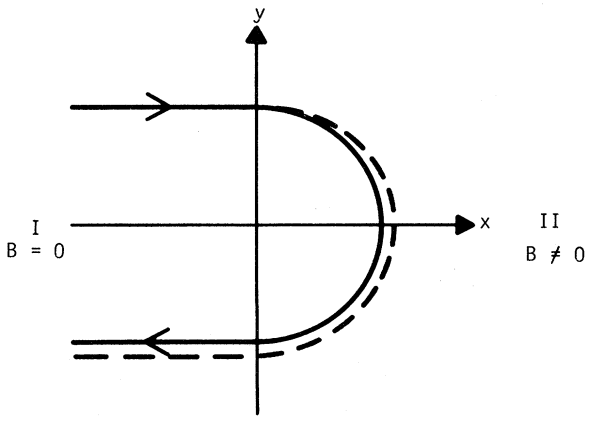

FIG. 5. Deflection of a charged particle (solid line) and a charged particle with a permanent dipole moment (dashed line), as explained in the text. The separation of the trajectories is exaggerated for illustration.

deflection. Anticipating that $|\delta\underline{R}_\perp| \ll |\underline{R}_\perp|$, this requires that $\underline{\mu}$ always point in the radial direction of the unperturbed trajectory,

$$\underline{\mu}=\mu(\sin\omega t, \cos\omega t, 0) . \tag{A35}$$

After time T, the correction $\delta\underline{R}_\perp$ then amounts to

$$\delta\underline{R}_\perp \cong \frac{\mu B}{Mc}\int_0^T (\hat{x}\cos\omega t - \hat{y}\sin\omega t)dt$$
$$= -2\frac{\mu}{e}\hat{y} , \tag{A36}$$

which is independent of B. [This is because T depends upon B through Eq. (A32).] The fractional change in the radius upon traversing the semicircle is thus

$$\left|\frac{\delta\underline{R}_\perp}{\underline{R}_\perp}\right| \cong \frac{2\mu}{e}\frac{\omega}{v_i} = \frac{2\mu B}{Mcv_i}$$
$$= 4\times 10^{-5}\frac{B}{Mv_i} , \tag{A37}$$

with M in units of the proton mass, B in Gauss, v_i in cm sec^{-1} and $\mu=1$ D$=10^{-18}$ esu. For reasonable laboratory parameters, we might take $B=15$ kG and $v_i=10^4$ cm sec^{-1}. This leads to a fractional displacement of

$$\left|\frac{\delta\underline{R}_\perp}{\underline{R}_\perp}\right| = 6\times 10^{-5}/M , \tag{A38}$$

which is very small. Since this is an upper bound on the deviation, we see that the CM motion should not differ detectably from the single-particle orbit through the field region.

APPENDIX B: TWO-BODY HAMILTONIAN AND UNITS

In this appendix, the multipolar Hamiltonian for two particles is reduced to more familiar form, and the units used in the calculations of Secs. IV and V are summarized.

The linear transformation $\underline{\underline{D}}$ of Sec. III.B is, using Eqs. (3.20)—(3.22),

$$\underline{\underline{D}} = \begin{pmatrix} \left[\frac{m_1 m_2}{a_1 M}\right]^{1/2} & -\left[\frac{m_1 m_2}{a_1 M}\right]^{1/2} \\ \frac{m_1}{M} & \frac{m_2}{M} \end{pmatrix} . \tag{B1}$$

Making the conventional choice

$$\mu \equiv a_1 = \frac{m_1 m_2}{M} \tag{B2}$$

yields, from Eqs. (3.18) and (3.19),

$$\underline{\rho} \equiv \underline{R}_1 = \underline{r}_1 - \underline{r}_2 ,$$
$$\underline{R} \equiv \underline{R}_2 = \frac{m_1}{M}\underline{r}_1 + \frac{m_2}{M}\underline{r}_2 ,$$
$$\underline{\pi} \equiv \underline{P}_1 = \frac{m_2}{M}\underline{p}_1 - \frac{m_1}{M}\underline{p}_2 , \tag{B3}$$
$$\underline{P} \equiv \underline{P}_2 = \underline{p}_1 + \underline{p}_2 .$$

The multipolar Hamiltonian H of Eq. (3.40) can be separated as

$$H = H_{||} + \mathscr{H} , \tag{B4}$$

$$H_{||} = \frac{1}{2M}P_z^2 - eE_{||}Z , \tag{B5}$$

$$\mathscr{H} = \frac{1}{2M}\left[\underline{P}_\perp - \frac{e}{2c}\underline{B}\times\underline{R}_\perp - \frac{\varepsilon_{12}}{c}\underline{B}\times\underline{\rho}\right]^2 - e\underline{E}_\perp\cdot\underline{R}_\perp$$
$$+ \frac{1}{2\mu}\left[\underline{\pi} - \frac{\varepsilon_{11}}{2c}\underline{B}\times\underline{\rho}\right]^2 - \varepsilon_{12}\underline{E}\cdot\underline{\rho} + \frac{e_1 e_2}{\rho} , \tag{B6}$$

where the elements of $\underline{\underline{\varepsilon}}$ are readily found from Eqs. (3.24), (B1), and (B2):

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} e_1\left[\frac{m_2}{M}\right]^2 + e_2\left[\frac{m_1}{M}\right]^2 & e_1\frac{m_2}{M} - e_2\frac{m_1}{M} \\ e_1\frac{m_2}{M} - e_2\frac{m_1}{M} & e \end{pmatrix} . \tag{B7}$$

We shall consider only the reduced Hamiltonian $\mathscr{H}$, which contains no reference to the CM coordinate Z. The symbol Z is hereafter used in conformity with tradition to denote nuclear charge. Particle 1 is taken as an electron with charge $-q$ and particle 2 as a nucleus with charge Zq,

$$e_1 = -q ,$$
$$e_2 = Zq . \tag{B8}$$

The matrix $\underline{\underline{\varepsilon}}$ may now be expressed as

$$\underline{\underline{\varepsilon}} = q\begin{pmatrix} -\frac{1-Z\delta^2}{(1+\delta)^2} & -\frac{1+Z\delta}{1+\delta} \\ -\frac{1+Z\delta}{1+\delta} & Z-1 \end{pmatrix} , \tag{B9}$$

where δ is the dimensionless mass ratio,

$$\delta = \frac{m_1}{m_2} . \tag{B10}$$

The infinite-nuclear-mass limit, $m_2\to\infty$ with m_1 fixed, then corresponds to the limit $\delta\to 0$.

The reduced Hamiltonian $\mathscr{H}$ becomes, after expanding the transverse CM kinetic energy,

$$\mathscr{H} = \frac{1}{2M}\left[\underline{P}_\perp - \frac{q(Z-1)}{2c}\underline{B}\times\underline{R}_\perp\right]^2 - q(Z-1)\underline{E}_\perp\cdot\underline{R}_\perp + \frac{1}{2\mu}\underline{\pi}^2 - \frac{Zq^2}{\rho} + q\frac{1+Z\delta}{1+\delta}\underline{E}\cdot\underline{\rho}$$
$$+ \frac{q}{Mc}\frac{1+Z\delta}{1+\delta}\left[\underline{P}_\perp - \frac{q(Z-1)}{2c}\underline{B}\times\underline{R}_\perp\right]\cdot\underline{B}\times\underline{\rho} + \frac{q}{2\mu c}\frac{1-Z\delta^2}{(1+\delta)^2}\underline{B}\cdot\underline{\rho}\times\underline{\pi} + \frac{q^2\alpha_4}{8\mu c^2}(\underline{B}\times\underline{\rho})^2 , \tag{B11}$$

where the last term is the sum of internal diamagnetic terms buried in the CM and relative kinetic energies. The constant α_4 is

$$\alpha_4=(1+\delta)^{-4}(1+4\delta+6Z\delta^2+4Z^2\delta^3+Z^2\delta^4)\ . \quad \text{(B12)}$$

It is to be noted that $\alpha_4=1$ for neutral systems ($Z=1$).

We now want to convert to a set of atomic units which coincide with those of Surmelian and O'Connell (1974) in the infinite-nuclear-mass limit. The unit of length here is the first Bohr radius for a two-body system of reduced mass μ and nuclear charge Zq,

$$a_0=\frac{\hbar^2}{\mu Z q^2}\ . \quad \text{(B13)}$$

(The common definitions of a_0 use either the reduced mass μ or the electron mass m_1, but both exclude the factor Z.)

Convenient measures of the electric and magnetic field strengths are, correspondingly,

$$E_0=\frac{qZ}{a_0^2}=\frac{\mu^2Z^3q^5}{\hbar^4}\ , \quad \text{(B14)}$$

$$B_0=\frac{\hbar c}{qa_0^2}=\frac{\mu^2Z^2q^3c}{\hbar^3}\ . \quad \text{(B15)}$$

For atomic hydrogen, these have the values $E_0=5.136\,61\times10^9$ V cm^{-1}, and $B_0=2.347\,97\times10^9$ G according to the physical constants of Cohen and Taylor (1973). We define the dimensionless vectors

$$\underline{\mathscr{F}}=\frac{\underline{E}}{E_0}\ , \quad \text{(B16)}$$

$$\underline{\gamma}=\frac{\underline{B}}{B_0}\ . \quad \text{(B17)}$$

The magnitude of $\underline{\mathscr{F}}$ is the ratio of the external electric field strength to the internal one due to the nucleus at a distance of one Bohr radius. From Eqs. (2.60) and (B15), $\gamma=\lambda^2/a_0^2$, the square of the ratio of the cyclotron and Bohr radii.

Using Eqs. (B16), (B17), and

$$\underline{\rho}'=\frac{\underline{\rho}}{a_0}\ , \quad \text{(B18)}$$

$$\underline{R}_\perp'=\frac{\underline{R}_\perp}{a_0}\ , \quad \text{(B19)}$$

we see that $\mathscr{H}$ becomes

$$\mathscr{H}=\frac{\hbar^2}{\mu a_0^2}\mathscr{H}' \quad \text{(B20)}$$

$$\mathscr{H}'=\frac{\mu}{2M}\left[-i\nabla_{R_\perp'}-\frac{Z-1}{2}\underline{\gamma}\times\underline{R}_\perp'\right]^2-(Z-1)\underline{\mathscr{F}}_\perp\cdot\underline{R}_\perp'-\tfrac{1}{2}\nabla_{\rho'}^2-\frac{1}{\rho'}+\frac{1+Z\delta}{1+\delta}\underline{\mathscr{F}}\cdot\underline{\rho}'$$
$$-\frac{i}{2}\frac{1-Z\delta^2}{(1+\delta)^2}\underline{\gamma}\cdot\underline{\rho}'\times\nabla_{\rho'}+\frac{\alpha_4}{8}(\underline{\gamma}\times\underline{\rho}')^2+\frac{\mu}{M}\frac{1+Z\delta}{1+\delta}\left[-i\nabla_{R_\perp'}-\frac{Z-1}{2}\underline{\gamma}\times\underline{R}_\perp'\right]\cdot\underline{\gamma}\times\underline{\rho}'\ . \quad \text{(B21)}$$

The primed quantities $\underline{\rho}'$, $\underline{R}_\perp'$, and $\mathscr{H}'$ are the same as the unprimed ones if the units are defined by

$$\mu=\hbar=a_0=1\ . \quad \text{(B22)}$$

The unit of energy is then

$$\mathscr{E}_0=\frac{\hbar^2}{\mu a_0^2}=\frac{\mu Z^2q^4}{\hbar^2}\ . \quad \text{(B23)}$$

The primes are hereafter dropped.

Neutral case ($Z=1$)

For $Z=1$, $\mathscr{H}$ reduces to

$$\mathscr{H}=-\frac{1}{2M}\nabla_{R_\perp}^2-\tfrac{1}{2}\nabla_\rho^2-\frac{1}{\rho}+\underline{\mathscr{F}}\cdot\underline{\rho}-\frac{i}{2}\frac{1-\delta}{1+\delta}\underline{\gamma}\cdot\underline{\rho}\times\nabla_\rho$$
$$+\tfrac{1}{8}(\underline{\gamma}\times\underline{\rho})^2-\frac{i}{M}\nabla_{R_\perp}\times\underline{\gamma}\cdot\underline{\rho}\ , \quad \text{(B24)}$$

which is independent of $\underline{R}_\perp$. Operating upon the plane-wave $\exp(i\underline{K}_\perp\cdot\underline{R}_\perp)$, $-i\nabla_{R_\perp}$ is replaced by $\underline{K}_\perp$ everywhere in $\mathscr{H}$. Subtracting the resulting constant term $K_\perp^2/2M$, we arrive at the effective internal Hamiltonian h of Eq. (4.11),

$$h=-\tfrac{1}{2}\nabla_\rho^2-\frac{1}{\rho}+\left[\underline{\mathscr{F}}+\frac{1}{M}\underline{K}\times\underline{\gamma}\right]\cdot\underline{\rho}$$
$$-\frac{i}{2}\frac{1-\delta}{1+\delta}\underline{\gamma}\cdot\underline{\rho}\times\nabla_\rho+\tfrac{1}{8}(\underline{\gamma}\times\underline{\rho})^2\ . \quad \text{(B25)}$$

Ionic case ($Z>1$)

We can express the Hamiltonian for the ionic problem in terms of the operators a, $a^\dagger$, b, and $b^\dagger$ of Eqs. (2.65),

$$\mathscr{H}=\alpha_1\gamma(a^\dagger a+\tfrac{1}{2})-\left[\frac{Z-1}{2\gamma}\right]^{1/2}[(a+b^\dagger)(\mathscr{F}_x-i\mathscr{F}_y)+(a^\dagger+b)(\mathscr{F}_x+i\mathscr{F}_y)]$$
$$-\tfrac{1}{2}\nabla_\rho^2-\frac{1}{\rho}+\frac{1+Z\delta}{1+\delta}\underline{\mathscr{F}}\cdot\underline{\rho}-i\alpha_2\underline{\gamma}\cdot\underline{\rho}\times\nabla_\rho-\alpha_3[a(x-iy)+a^\dagger(x+iy)]+\frac{\alpha_4}{8}(\underline{\gamma}\times\underline{\rho})^2\ , \quad \text{(B26)}$$

where we have defined the constants

$$\alpha_1=\frac{Z-1}{M}\ , \tag{B27}$$

$$\alpha_2=\frac{1}{2}\frac{1-Z\delta^2}{(1+\delta)^2}\ , \tag{B28}$$

$$\alpha_3=\frac{1+Z\delta}{M(1+\delta)}\left[\frac{Z-1}{2}\right]^{1/2}\ , \tag{B29}$$

for convenience in Secs. V.C and V.D. Note that, in the present units, the cyclotron radius and frequency are

$$\lambda=(\hbar c/eB)^{1/2}=[(Z-1)\gamma]^{-1/2}\ , \tag{B30}$$

$$\omega=eB/Mc=[(Z-1)\gamma]/M\ . \tag{B31}$$

For vanishing electric field, the recursion relations in Eqs. (2.69) may readily be used upon the wave function as expanded in Sec. V.B, resulting in the coupled equations given in Eqs. (5.55)—(5.59).

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