PHYSICAL REVIEW A VOLUME 4, NUMBER 2 AUGUST 1971

Euler-Lagrange Optimization of Plane-Wave Factors*

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(Received 22 March 1971)

The Euler-Lagrange variational method is applied to plane-wave factors as they appear in the parametric time-dependent Schrödinger-equation model for atom-atom scattering. The resulting Euler-Lagrange equations provide a prescription for determining a general plane-wave-factor function of the electron coordinates and time.

I. INTRODUCTION

Plane-wave factors arise in scattering theory for two related reasons: (i) Channel states should be described in an asymptotically separable coordinate system to facilitate construction of the S matrix, and (ii) a finite basis used in the expansion of internal degrees of freedom may be greatly improved by a proper inclusion of terms which build in linear momentum. The analysis presented here is in the parametric time-dependent Schrödinger-equation approximation, which itself must be obtained from a more general description of the collision problem.

The physical system used in discussion might be H_2^+ or HeH^{++}, both of which are three-body problems with greatly varying masses, possessing excitation, rearrangement, and ionization channels. We shall take the two nuclei to be A and B with masses m_A and m_B and the electron e with mass m. Consider a space-referenced coordinate system with $\vec{\mathrm{R}}$ measured from A to B and electron coordinate $\vec{\mathrm{r}}$ measured from the center of mass of A and B. The Schrödinger equation in the barycentric subspace with the kinetic energy written in the above coordinates is

$$\left(-\frac{\hbar^2}{2\mu_B^A}\nabla_R^2-\frac{\hbar^2}{2\mu_{AB}^e}\nabla_r^2+V_{eA}+V_{eB}+V_{AB}-E\right)\psi(\vec{\mathrm{r}},\vec{\mathrm{R}})=0\,, \quad (1)$$

$$\mu_j^i=m_i m_j/(m_i+m_j)\,,$$

which we assume corresponds to the parametric equation

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2+V_{eA}+V_{eB}+V_{AB}-i\hbar\frac{\partial}{\partial t}\right)\psi(\vec{\mathrm{r}},t)=0\,, \quad (2)$$

with an imposed classical motion of the nuclei A and B. The relation of (2) to (1) has been studied in several contexts,[1-5] most of which include the three-dimensional semiclassical approximation as an intermediate step.

Equation (2) and its many-electron generalizations have been extensively used in the literature[6,7]; we adopt it as an adequate equation of motion for the electrons which describes them as responding to an imposed classical motion of the nuclei, this being either an averaged,[1,3,8] an elastic,[9] or a rectilinear[10-12] trajectory. The solution of (2) is a well defined but difficult problem of its own right, this alone being the concern of the present paper. The general approach to (2) is to make an expansion

$$\psi^i(\vec{\mathrm{r}},t)=\sum_n C_{ni}(t)\,\chi_n(\vec{\mathrm{r}},t) \quad (3)$$

and obtain a coupled set of first-order differential equations in time by projecting with members of the set χ_n. Bates[13] and Bates and McCarroll[14] noted that, if the χ_n are atomic orbitals centered on A or B, or if they are Born-Oppenheimer states of the electronic Hamiltonian (perturbed stationary states), the differential equations do not decouple at $|t|\to\infty$. To remedy this situation in the context of Eq. (2) with rectilinear trajectories, the plane-wave-factor concept was introduced, whereupon expansion (3) is rewritten as

$$\psi^i(\vec{\mathrm{r}},t)=\sum_n C_{ni}^A(t)\,\chi_n^A(\vec{\mathrm{r}},t)\exp[-i\gamma_{AB}^B(m/\hbar)vz]$$
$$+\sum_n C_{ni}^B(t)\chi_n^B(\vec{\mathrm{r}},t)\exp[i\gamma_{AB}^A(m/\hbar)vz]\,,$$

where $\gamma_{jk}^i=m_i/(m_j+m_k)$, positive z lies along the relative collision-velocity vector, and v is the relative constant collision velocity. The χ_n^j are either atomic basis functions on nucleus j, or combinations of Born-Oppenheimer states chosen such that they localize into an atomic state on nucleus j at large separation.[14] This ensures decoupling as $|t|\to\infty$ and a unique determination of the amplitudes for excitation and rearrangement. The atomic-state-expansion version of Eq. (4) has been successfully applied to one- and two-electron systems at energies above several keV and an equivalence to the Born approximation has also been shown in the weak-coupling limit.[13] The molecular-state-expansion version of Eq. (4) has not yet received extensive investigation.

A different plane-wave factor has been developed by Schneiderman and Russek[15] and by Levy and Thorson[16] in which the expansion

$$\psi^i(\vec{r}, t) = [\sum_n C_{ni}(t)\, \chi_n(\vec{r}, t)] \times \exp[if(\vec{r}, t)(m/\hbar)\vec{v}\cdot\tfrac{1}{2}\vec{r}] \quad (5)$$

is used with certain conditions placed on $f(\vec{r}, t)$.[15] For the H_2^+ system, for example, $f(\vec{r}, t) \to \pm 1$ as $|t| \to \infty$, depending on whether the electron is nearer B or A. References 15 and 16 discuss particular functional forms of $f(\vec{r}, t)$ in detail and explain the motivations for expansion (5) as opposed to (4)—primarily orthogonality and flexibility. The important difference between (4) and (5) is that form (5) involves a single flexible factor for the whole wave function while (4) associates a different plane-wave factor with each atomic center. A probable serious defect of form (5) is that it may not agree with the Born exchange cross section in a weak-coupling approximation at high energy. However, the use of (5) is only proposed for the low-energy region[16] where one must calculate a solution of the Schrödinger equation rather than use low-order perturbation theory.

It is characteristic of expansions (4) and (5) that the plane-wave factors are chosen *a priori;* they must satisfy certain conditions, primarily to ensure decoupling at large separation, but are not determined in any other way. Nevertheless, it is known that their form influences calculations considerably.[16] The purpose of the present paper is to search for optimum choices of plane-wave factors using the Euler-Lagrange variational method. The investigation is not exhaustive, but the results illuminate the nature of the problem and should provide guidance for further work.

Section II outlines the Euler-Lagrange method for the optimization of three forms of plane-wave factors, concentrating mainly on the mathematics of the procedure. Section III is devoted to discussion and interpretation.

II. EULER-LAGRANGE METHOD

Cheshire[17] and McCarroll, Piancentini, and Salin[18] have used the Euler-Lagrange variational method[19] to optimize the effective nuclear charge (exponential screening parameter) in an atomic-orbital-expansion basis of form (4). This seems to be a very powerful technique for introducing nonlinear variations into the usual set of coupled differential equations obtained by basis projection or, equivalently, by varying only the linear expansion coefficients $C_{ni}(t)$.[17]

After considering several forms of plane-wave factors and the resulting relations derived by optimization, only a few cases seem (to us) worth investigating here. This will now be done, leaving the discussion of choice aside until the equations are evident. We write (2) as

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2 + V(\vec{r}, \vec{R}) - i\hbar\frac{\partial}{\partial t}\right)\psi(\vec{r}, t) = 0 \ , \quad (6)$$

and know $\vec{R} = \vec{R}(t)$ as the imposed nuclear motion. The Lagrange density for this Schrödinger equation is[19]

$$L(\vec{r}, t) = -\frac{\hbar^2}{2m}\vec{\nabla}\psi^*\cdot\vec{\nabla}\psi - \frac{\hbar}{2i}(\psi^*\dot{\psi} - \dot{\psi}^*\psi) - \psi^* V\psi \ . \quad (7)$$

The Euler-Lagrange equations are determined from the requirement that the integral

$$I = \int_{-\infty}^{\infty} dt \int d^3r\, L(\vec{r}, t) \quad (8)$$

be stationary with respect to arbitrary variations in the functions of time and/or coordinates which are to be optimized. In this analysis we assume that there are no variations on the boundaries, which allows a simplification in the derivation of the Euler-Lagrange equations by means of an integration of parts.[17,19]

The first trial form we investigate contains only time-dependent functions to be optimized, $N(t)$ and $\vec{\lambda}(t)$; we write

$$\psi(\vec{r}, t) = N(t)\,\chi(\vec{r}, t)\, e^{i\vec{\lambda}(t)\cdot\vec{r}} = N(t)\phi(\vec{r}, t); \quad (9)$$

$\chi(\vec{r}, t)$ is given, either as a fixed linear approximation like (3) or a single basis member of that set; χ and ϕ are each normed to unity for all time; $\vec{\lambda}(t)$ is real, but $N(t)$ is complex. Introducing

$$\mathfrak{L}(t) = \int d^3r\, L(\vec{r}, t) \ , \quad (10)$$

we find that the Euler-Lagrange equations are

$$\frac{\partial\mathfrak{L}}{\partial\lambda_i} - \frac{d}{dt}\left(\frac{\partial\mathfrak{L}}{\partial\dot{\lambda}_i}\right) = 0, \quad i = 1, \ldots, 5 \quad (11)$$

where λ_i denotes the set of three vector components of $\vec{\lambda}$ and N and N^*. Equation (11) may be replaced by

$$\vec{\nabla}_\lambda\mathfrak{L} - \frac{d}{dt}(\vec{\nabla}_{\dot{\lambda}}\mathfrak{L}) = 0 \ , \quad (12)$$

$$\frac{\partial\mathfrak{L}}{\partial N^*} - \frac{d}{dt}\left(\frac{\partial\mathfrak{L}}{\partial\dot{N}^*}\right) = 0 \quad (13)$$

with no loss of information. Introducing (9) into (7) and evaluating (10), one can show that (13) implies, up to a multiplicative constant,

$$N(t) = \exp\left(-\frac{i}{\hbar}\int^t dt' \left\langle\phi\left|H - i\hbar\frac{\partial}{\partial t'}\right|\phi\right\rangle\right) \ . \quad (14)$$

From (12) one will arrive at

$$\frac{\hbar}{m}\vec{\lambda}(t)=\frac{d}{dt}\left(\int d^3r\,\chi^*\vec{r}\,\chi\right)-\int d^3r\,\vec{f}\ , \qquad (15)$$

where $\vec{f}=(i\hbar/2m)(\chi\vec{\nabla}\chi^*-\chi^*\vec{\nabla}\chi)$ is the flux density of χ. Equation (15) may be written as

$$\frac{\hbar}{m}\vec{\lambda}(t)=\frac{d}{dt}\langle\chi|\vec{r}|\chi\rangle-\langle\chi|-i\frac{\hbar}{m}\vec{\nabla}|\chi\rangle\ , \qquad (16)$$

which allows the interpretation of $(\hbar/m)\vec{\lambda}(t)$: It is the time derivative of the expectation of electron position relative to the center of mass of A, B less the expectation of electron velocity relative to the center of mass of A, B. These results will be discussed in the following section.

We now develop the equations for optimization of a coordinate-dependent general plane-wave factor of the form indicated in (5). Our trial form is

$$\psi(\vec{r},t)=N(t)\,\chi(\vec{r},t)\,e^{i\alpha(\vec{r},t)}=N(t)\,\phi(\vec{r},t)\ . \qquad (17)$$

N is complex, α is real, and χ and ϕ are both normed for all time. As before, the Euler-Lagrange equation for $N(t)$ is

$$\frac{\partial\mathcal{L}}{\partial N^*}-\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{N}^*}\right)=0\ , \qquad (18)$$

giving, up to a constant, the same result as (14), with $\phi(\vec{r},t)$ now $\chi e^{i\alpha}$. The Euler-Lagrange equation for $\alpha(\vec{r},t)$ is

$$\frac{\partial L}{\partial\alpha}-\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial\dot{\alpha}}\right)-\frac{\partial}{\partial x}\left(\frac{\partial L}{\partial\alpha_x}\right)-\frac{\partial}{\partial y}\left(\frac{\partial L}{\partial\alpha_y}\right)-\frac{\partial}{\partial z}\left(\frac{\partial L}{\partial\alpha_z}\right)=0\ , \qquad (19)$$

written in Cartesian coordinates with $\alpha_r=\partial\alpha/\partial r$. This will lead to

$$\frac{\partial}{\partial t}(\chi^*\chi)+\vec{\nabla}\cdot\left(\chi^*\chi\frac{\hbar}{m}\vec{\nabla}\alpha+\vec{f}\right)=0\ , \qquad (20)$$

where, again, $\vec{f}=(i\hbar/2m)(\chi\vec{\nabla}\chi^*-\chi^*\vec{\nabla}\chi)$. Letting $\rho=\chi^*\chi=A^2$, $\beta=(\hbar/m)\alpha$, and $\gamma=A\dot{\beta}$, one easily arrives at

$$\dot{\rho}+\vec{\nabla}\cdot(\rho\vec{\nabla}\beta+\vec{f})=0\ , \qquad (21)$$

$$-\nabla^2\gamma+(\nabla^2A/A)\gamma=2\dot{A}+\vec{\nabla}\cdot\vec{f}/A\ . \qquad (22)$$

The solution of the fluid continuity equation (21) for the vector field $\vec{\nabla}\beta$ is unique up to $\vec{\nabla}\beta=(1/\rho)\times\vec{\nabla}\times\vec{V}$, where $\vec{V}$ is arbitrary since $\vec{\nabla}\cdot\vec{\nabla}\times\vec{V}\equiv0$. However, the vector field $\vec{\nabla}\beta$ is a gradient, which restricts this nonuniqueness in a complicated manner. Equation (22) is more lucid: $\gamma=A$ is the only homogeneous solution (∇^2A/A has the spatial character of an eigenvalue problem) and we note that

$$2\int d^3r\,A\dot{A}=\int d^3r\,\frac{d}{dt}(\chi^*\chi)=0\ , \qquad (23)$$

$$\int d^3r\,A\vec{\nabla}\cdot\frac{\vec{f}}{A}=\int d^3r\,\vec{\nabla}\cdot\vec{f}=\int d^2S\,\hat{e}_s\cdot\vec{f}=0, \qquad (24)$$

since $\vec{f}$ vanishes at large $\vec{r}$. Knowing that the homogeneous solution is orthogonal to the right-hand side of (22), we can construct the general solution of (22) in terms of the eigenfunctions of

$$(-\nabla^2+\nabla^2A/A-E_n)Z_n=0,\quad n=0,\ldots \qquad (25)$$

with $Z_0=A$, $E_0=0$, as

$$\gamma(\vec{r},t)=C_0A+\sum_{n=1}^{\infty}Z_n\frac{\langle Z_n|2\dot{A}+\vec{\nabla}\cdot\vec{f}/A\rangle}{E_n}\ , \qquad (26)$$

with $C_0=C_0(t)$ arbitrary. We find

$$\beta(\vec{r},t)=\frac{\hbar}{m}\alpha=C_0+\frac{1}{A}\sum_{n=1}^{\infty}Z_n\frac{\langle Z_n|2\dot{A}+\vec{\nabla}\cdot\vec{f}/A\rangle}{E_n}\ . \qquad (27)$$

Without any attempt at rigor, we take this to be the most general possible solution for the determination of a plane-wave factor of unspecified functional dependence. However, it is of such complexity as to be unsuited for practical calculation, and, moreover, the next paragraph gives an optimum means of approximating the solution of Eq. (20).

The third and last derivation treats the optimization of a factor containing a set of time-dependent variational parameters $\{A_n(t)\}$; letting

$$\psi(\vec{r},t)=N(t)\,\chi(\vec{r},t)\exp[i\alpha(\vec{r},t,\{A_n(t)\})],\quad n=1,\ldots,N \qquad (28)$$

with χ given, α real, and N complex, we want the Euler-Lagrange equations for $N(t)$ and the $A_i(t)$, $i=1,\ldots,N$. Note that α itself is not being varied, only the $\{A_n(t)\}$, but with the functional dependence of α on the $\{A_n\}$ left unspecified, we set

$$\dot{\alpha}=\frac{\partial}{\partial t}\alpha(\vec{r},t,\{A_n\}),\quad \alpha_{A_m}=\frac{\partial}{\partial A_m}\alpha(\vec{r},t,\{A_n\}), \qquad (29)$$

$$\rho=\chi^*\chi,\quad \vec{f}=(i\hbar/2m)(\chi\vec{\nabla}\chi^*-\chi^*\vec{\nabla}\chi)\ .$$

The time-dependent energy factor N will again be of form (14), and for simplicity we drop it from consideration and have the Lagrangian density

$$L(\vec{r},t)=-\frac{\hbar^2}{2m}\vec{\nabla}\chi^*\cdot\vec{\nabla}\chi-\hbar\vec{\nabla}\alpha\cdot\vec{f}-\frac{\hbar^2}{2m}\vec{\nabla}\alpha\cdot\vec{\nabla}\alpha\rho-\frac{\hbar}{2i}(\chi^*\dot{\chi}-\dot{\chi}^*\chi)-\hbar\rho\dot{\alpha}-\hbar\rho\sum_{n=1}^{N}\dot{A}_n\alpha_{A_n}\ . \qquad (30)$$

The Euler-Lagrange equations are in terms of $\partial L/\partial A_m$ and $\partial L/\partial \dot{A}_m$. They reduce to

$$\int d^3r \{\vec{\nabla}\alpha_{A_m} \cdot [(\hbar/m)\rho\vec{\nabla}\alpha + \vec{f}] - \alpha_{A_m}\dot{\rho}\} = 0,$$

$$m = 1, \ldots, N \quad (31)$$

or, integrating by parts,

$$\int d^3r\, \alpha_{A_m}\{\vec{\nabla} \cdot [(\hbar/m)\rho\vec{\nabla}\alpha + \vec{f}] + \dot{\rho}\} = 0\,,$$

$$m = 1, \ldots, N. \quad (32)$$

Suppose that α had been developed in a linear expansion:

$$\alpha(\vec{r}, t, \{A_m\}) = \sum_{i=1}^{N} A_i(t)\,\varphi_i(\vec{r}, t)\,,$$

$$\alpha_{A_m} = \varphi_m\,, \quad \vec{\nabla}\alpha_{A_m} = \vec{\nabla}\varphi_m\,, \quad (33)$$

$$\vec{\nabla}\alpha = \sum_{i=1}^{N} A_i(t)\vec{\nabla}\varphi_i(\vec{r}, t)\;;$$

it is then evident that the $N\times N$ system of linear algebraic equations, (31) or (32), is exactly that obtained by inserting the expansion for α into (20) or (21) and projecting with members of the basis, allowing an explicit solution for the A_n in terms of ρ and $\dot{\rho}$.[20]

Thus far the function χ appearing in Eqs. (9), (17), and (28) has been fixed; that is to say, no allowance has been made for it to be optimized during the collision. If we are seeking an optimum plane-wave factor to associate with an individual basis function χ_n, solutions (15), (27), and (32) (with a linear expansion for α) are complete as they stand. The general case, however, is that χ itself will be a linear superposition with time-dependent coefficients to be optimized. In particular, this is necessitated by the form of Eq. (5) and produces a *coupled* relation between the equations determining the plane-wave factor, i.e., Eqs. (15), (27), and (32), and those determining the coefficients in χ. The mechanics of solving the total problem of a linear expansion for α used in conjunction with one for χ will now be outlined.[21] The wave function for initial state i is expanded as

$$\psi^i = \left(\sum_{n=1}^{N_1} C_{ni}(t)\chi_n\right) \exp\left(i\sum_{n=1}^{N_2} A_{ni}(t)\,\varphi_n\right) = \chi e^{i\alpha}. \quad (34)$$

We let $\underline{C}$ denote the matrix of $C_{ni}(N_1\times N_1)$ and $\underline{A}$ denote the matrix of $A_{ni}(N_2\times N_2)$. Variation of $\underline{C}$ leads to the coupled set of differential equations obtained by projection with $\chi_m e^{i\alpha}$ on the Schrödinger equation. We express this functional relation as

$$\dot{\underline{C}} = f(\underline{C}, \underline{A}, \dot{\underline{A}})\,. \quad (35)$$

Equation (32) may be solved for $\underline{A}$,

$$\underline{A} = h(\underline{C}, \dot{\underline{C}})\,. \quad (36)$$

Together, (35) and (36) constitute a set of implicit nonlinear differential equations for $\underline{A}$ and $\underline{C}$. We can base an integration method on the following. Suppose $\underline{C}$, $\dot{\underline{C}}$, $\underline{A}$, and $\dot{\underline{A}}$ are known for a series of time intervals up to and including t_0. A high-order integration method will give $\underline{C}_1$ at $t_1 = t_0 + \Delta t$; then essentially we guess (extrapolate) $\dot{\underline{C}}_1$ and calculate $\underline{A}_1$ by (36) and $\dot{\underline{A}}_1$ by backward difference from $\underline{A}_1$ and $\underline{A}_0$; these are then used to evaluate a new $\dot{\underline{C}}_1$ by (35) and the cycle is repeated until $\dot{\underline{C}}_1$, $\underline{A}_1$, and $\dot{\underline{A}}_1$ stabilize. Convergence may require some averaging between cycles. None of this iterative process necessitates new evaluation of the integrals involved in state projection or in (32).

In general, one can say that the solution of Eq. (2) by a trial wave function containing time-dependent variational functions C_n will necessitate computing all of them throughout the collision and that all will be coupled to one another.[21] We are not obligated to carry out the full variation of all the C_n together though, and we can obtain meaningful equations by approximations to the stationarity requirements.

III. DISCUSSION

The main limitation of the preceding results is that they are based on trial solutions of the form $\chi e^{i\alpha}$. This is consistent with the structure expressed in Eq. (5), but not with that in Eq. (4). We are obviously most able to treat form (5) and do so now.

To a certain extent there is a compensatory relation between χ and α which is, of course, reflected in the coupling between them as illustrated in Eqs. (35) and (36). Since α is real, we cannot set $\chi = 1$, say, and expect $e^{i\alpha}$ to reproduce ψ; however, we could set $\alpha = 0$ and expect a complete basis for χ to reproduce ψ precisely. This complete set for χ would make the α solution indeterminate, but with any particular approximations to χ and α, the Euler-Lagrange equations are just coupled. Knowing the states one wishes to use as a basis for χ and the character of α, one may augment the χ basis with a group of pseudostates[12] which have the ability to efficiently describe "moving" states. By this we mean that, for example, the expansion of the moving hydrogenic $1s$ orbital, $\pi^{1/2}e^{-r}e^{i\vec{\kappa}\cdot\vec{r}}$, in the hydrogenic basis set is not complete in the first power of κ until the continuum is included. However, a basis consisting of an increasing degree set multiplying e^{-r} will progressively include more powers of κ as it in-

creases in size. Thus one can hope that a sufficiently flexible linear expansion in χ might eliminate the necessity of varying parameters in the plane-wave factors.

A general scheme for optimizing linear expansions for χ and for α was described in Eqs. (35) and (36) of the previous section. A one-term expansion for α for the H_2^+ system could be that of Schneiderman and Russek, [15]

$$\alpha(\vec{r}, t, A(t)) = A(t)\dot{\vec{R}} \cdot \vec{r}\,\hat{r} \cdot \hat{R} \ , \tag{37}$$

where our $A(t)$ replaces their $1/(1+a/R^2)$. From Eq. (32) one has the equation determining the optimum $A(t)$,

$$A(t)(\hbar/m)\int d^3r\, D(\vec{\nabla}\rho \cdot \vec{\nabla}D + \rho\vec{\nabla}^2 D) = -\int d^3r\, D(\vec{\nabla}\cdot\vec{f} + \dot{\rho}) \ , \tag{38}$$

where $D = \dot{\vec{R}} \cdot \vec{r}\,\hat{r} \cdot \hat{R}$. Although Eq. (38) is readily solved for $A(t)$, the solution retains the complexity explained in Eqs. (35) and (36). A simplification which might be valuable in cases of weak coupling would be to determine $A(t)$ from the part of χ which describes the initial state rather than the whole χ. This $A(t)$ would be used in Eq. (35) with no further improvement. If one considers the velocity field $(\hbar/m)\vec{\nabla}\alpha$ as a reasonable picture of the electron motion, the high-energy limit indicates that we need an additional degree of freedom in α that will allow the electron to move with the incident velocity whether it is near the incident nucleus or not. In addition, the heteronuclear system HeH^{++} necessitates a generalization that allows different large-R velocities for the two centers. The next step beyond (37) could be

$$\alpha(\vec{r}, t, A_1(t), A_2(t)) = A_1(t)\dot{\vec{R}} \cdot \vec{r}\, d_A + A_2(t)\dot{\vec{R}} \cdot \vec{r}\, d_B \ , \tag{39}$$

where d_A and d_B are weight functions centered on A and B. d_A and d_B could be $r_B^2/(r_A^2+r_B^2)$ and $r_A^2/(r_A^2+r_B^2)$, giving a generalization of Levy and Thorson's[16] plane-wave factor. The two coefficients are found for every t by solving a pair of coupled algebraic equations derived from Eq. (32).

We now consider expansions of the form of Eq. (4) where the plane-wave factors are inserted into the terms of the expansion. A potential generalization of (4) is

$$\psi^i(\vec{r}, t) = \chi_i^A \exp[i\vec{\lambda}^A(t)\cdot\vec{r}] + \chi_i^B \exp[i\vec{\lambda}^B(t)\cdot\vec{r}] \ , \tag{40}$$

where χ^j is a linear superposition of atomic, molecular, or pseudostates that localizes on center j. One can derive the Euler-Lagrange equations for $\vec{\lambda}^A$ and $\vec{\lambda}^B$, but, as far as we have seen, the simultaneous solution of these and the time-dependent equations for the linear coefficients in χ^A and χ^B would be laborious. Consequently we propose the following for the treatment of form (4): If the plane-wave factors are to be inserted into the individual terms of an expansion of ψ, they can be optimized for each term alone rather than in the whole coupled problem. As an example of this approximation, we take a two-center atomic-basis expansion with factors

$$\psi^i = \sum_{p=A,B}\sum_n C_{ni}^p(t)\chi_n^p(\vec{r}, t)\exp[i\vec{\lambda}_n^p(t)\cdot\vec{r}] \ . \tag{41}$$

We determine all $\vec{\lambda}_n^p(t)$ from the trial forms

$$\psi_n^p = \chi_n^p(\vec{r}, t)\exp[i\vec{\lambda}_n(t)\cdot\vec{r}] \tag{42}$$

and obtain from (16), (27), or (32)

$$\begin{aligned}(\hbar/m)\vec{\lambda}_n^A(t) &= -\gamma_{AB}^B\dot{\vec{R}}(t) \ , \\ (\hbar/m)\vec{\lambda}_n^B(t) &= \gamma_{AB}^A\dot{\vec{R}}(t) \ .\end{aligned} \tag{43}$$

With $\dot{\vec{R}} = \hat{e}_z v$ this optimization procedure leads directly to the plane-wave factors chosen for the atomic basis by Bates.

One cannot use this approximation approach to form (4) with a molecular-state expansion without caution; several difficulties arise. First, in homonuclear systems such as H_2^+, the association of a plane-wave factor of form $e^{i\vec{\lambda}(t)\cdot\vec{r}}$ with an individual eigenstate immediately gives $\vec{\lambda} = 0$ because the electron is equally dense around both centers. Second, again in H_2^+, the grouping of gerade and ungerade states into $g \pm u$ combinations makes possible a meaningful use of Bates's plane-wave factors as written in (4), but optimization of the corresponding trial form

$$\psi = (1/\sqrt{2})(\chi_g \pm \chi_u)\exp[i\vec{\lambda}^{\pm}(t)\cdot\vec{r}] \tag{44}$$

gives

$$\frac{\hbar}{m}\ \vec{\lambda}^{\pm} = \frac{1}{2}\frac{d}{dt}\langle \chi_g \pm \chi_u | \vec{r} | \chi_g \pm \chi_u \rangle \ , \tag{45}$$

which has a $1/R$ singularity at the united-atom limit due to the rotation of the asymmetrical charge density $|\chi_g \pm \chi_u|^2$ about the nuclear center of mass. Third and last, many-electron systems satisfying the Pauli principle in the molecular basis allow the electrons on both centers, which can result in the first and second difficulties above on a grander scale. Evidently, much more work is required on these problems. [22] To end on a positive observation, it should be mentioned that a system like HeH^{++}, because of localization at large R and an expectation of electron position that vanishes like R as $R \to 0$, has a well defined and perhaps

useful factor of form $\exp[i\vec{\lambda}(t)\cdot\vec{r}]$ for each molecular eigenstate.

IV. CONCLUDING REMARKS

The utility of the ideas presented remains to be tested in actual impact-parameter calculations. We feel that at present any new criterion for the choice of a plane-wave factor is of interest.

Note added in proof. C. F. Lebeda, W. R. Thorsen, and H. Levy II have recently investigated a means of choosing plane-wave factors for the H^+ on H ionization problem [Phys. Rev. A (to be published)].

ACKNOWLEDGMENT

Discussions with E. J. Shipsey on the Euler-Lagrange technique are gratefully acknowledged.

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*Work supported by the U. S. Atomic Energy Commission.

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[20]The choice $\varphi_1 = x$, $\varphi_2 = y$, $\varphi_3 = z$ allows this derivation to include the plane-wave factor $e^{i\vec{\lambda}\cdot\vec{r}}$ as a special case.

[21]The Euler-Lagrange equations for a trial solution ψ, containing real variational functions $C_n(t)$ in an arbitrary manner, are $0 = \mathrm{Re}[\int d^3r\, \psi_m^*(H - i\hbar\partial/\partial t)\psi]$, where $\psi_m = \partial\psi/\partial C_m$. This is a master set of equations containing all our results except Eq. (20).

[22]An interesting condition arises if one wishes to associate a general factor $\exp[\alpha(\vec{r}, t)]$ with each term of a molecular or rotating atomic-orbital expansion. If any of these basis functions (taken to be real) have nodal planes, the general solution (27) will be singular at these planes (where $A = 0$) under certain conditions. This is due to the infinite velocity required at a region of zero density in order to represent a finite flux flow across the region. If no such flux flow is required to satisfy the continuity equation (21), α is not singular.