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Optimised translation factors for low energy proton–hydrogen-atom collisions

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Abstract. The low energy proton–hydrogen-atom collision is described by an expansion in the $1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$ molecular orbitals accompanied by phase factors depending on the electronic coordinate, which considers the electronic density flux set up by the nuclear motion on each orbital. These phase factors are strongly dependent on the original state; their effect on the probability of excitation to the $2p_1$ level is smaller than that obtained by using plane-wave phase factors, which overestimate the electronic translational momentum. The resulting probability of charge exchange agrees with other theoretical approaches and also with experiment in the range of collision energies and impact parameters where an expansion in rotating molecular orbitals such as ours is justified.

1. Introduction

We will consider collisions between a proton and a ground-state hydrogen atom, where the internuclear velocity $\boldsymbol{v}$ is small compared with the characteristic velocity of the atomic electron. The protons will be taken as massive particles following classical trajectories; their relative coordinate $\boldsymbol{R}$ will then be a known function of time.

The motion of the electron remains to be solved, and will be described by the coordinate $\boldsymbol{r}$ relative to the midpoint between the protons. The Schrödinger equation has a time-dependent potential and because of the slowness of the nuclear motion, the natural basis for the wavefunction expansion is the set of eigenstates of the molecule H_2^+; in this way we are incorporating into each channel *the static deformation produced by the projectile on the atomic orbital.*

The nuclear motion causes the electron density in each channel to change with time, and an associated density flux that cannot be generated by a real wavefunction also exists. Asymptotically, the motion of each proton produces the whole translation of the atomic orbital $\chi_n(\boldsymbol{r} \pm \boldsymbol{R}/2)$ centred on the proton, and the travelling electron is represented exactly by the addition of a plane factor: $\exp(\pm i\boldsymbol{v}\boldsymbol{r}/2)\chi_n(\boldsymbol{r} \pm \boldsymbol{R}/2)$.

At finite internuclear distances R the atomic orbitals $\chi_n(\boldsymbol{r} \pm \boldsymbol{R}/2)$ are transformed into molecular states $\phi_n^{g,u}(\boldsymbol{r}, \boldsymbol{R})$ and the nuclear motion produces a time-dependent wavefunction. A change in the value of R then gives not only a translation of this function through space, but also modifies its dependence on the electronic coordinate $\boldsymbol{r}$. The electron density flux is a function of $\boldsymbol{r}$, and can be represented by a phase $f_n(\boldsymbol{r}, R)$, still with unknown $\boldsymbol{r}$ dependence, that incorporates into each channel *the dynamical action of the nuclear motion on the molecular orbital*: $\exp(\mathrm{i}f_n^{g,u}(\boldsymbol{r}, R)\phi_n^{g,u}(\boldsymbol{r}, R))$.

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Bates and McCarroll (1958) introduced plane-wave factors that provide the correct asymptotic behaviour of the wavefunction, and extended their validity to finite R; their basis functions are

$$\phi_n^{\pm} = \tfrac{1}{2}[(\phi_n^{g} + \phi_n^{u})\, e^{-ivz/2} \pm (\phi_n^{g} - \phi_n^{u})\, e^{ivz/2}].$$

In this way the phase factors describe the translation of the electron density, but its deformation with time is not taken into account. Crothers and Hughes (1978) generalise the basis set by introducing a parameter $f_n(R)$ in the plane-wave phases; this is equivalent to defining an effective velocity of translation $v_n(\text{eff}) = vf_n(R)$ determined through a variational procedure. This approach improves the description of the whole translation of the electron with either one of the protons, while the local electron flux produced by the time dependence of the molecular orbital is not taken into account since f_n does not depend on $\boldsymbol{r}$. Crothers and Hughes claim that to satisfy the uncertainty principle for both the electron coordinate and momentum the parameter f_n should not depend on $\boldsymbol{r}$. Now, since we consider the projectile to be a classical particle with a position given by $\boldsymbol{R}(t)$, our quantum system consists solely of the electron subject to a known external time-dependent potential. The probability of finding the electron in a certain point of space is given by the square of its wavefunction, while the probability of measuring a certain momentum for this electron is determined by the square of the Fourier transform of that wavefunction. A fundamental property arising from Fourier transforms is that the widths of the probability distributions in coordinate and momentum spaces are related so that they cannot both become small simultaneously, and more precisely, their product is always of the order of unity; this indicates that the position–momentum uncertainty principle is automatically satisfied, not only by the exact wavefunction of the one-electron system under discussion, but also by any approximate wavefunction proposed for the system (Messiah 1968). We then conclude, assuming that the nuclei behave as classical particles, that there are no restrictions on the form of the phase factors f_n made by the uncertainty relations. Furthermore, Crothers and Hughes use the same parameter $f_n(R)$ for the pair of functions $\Phi_n^{\pm}$; this is equivalent to assigning a plane-wave factor, with effective velocity of translation $v_n(\text{eff})$, to each term $\phi_n^{g} \pm \phi_n^{u}$ of the expansion. This approach is similar to an expansion in travelling atomic orbitals, with an optimised translation velocity where proper combinations of molecular orbitals replace the atomic states. We feel that this formulation is best suited to describe collisions at 'not-too-low' internuclear velocities, where the atomic characteristics of the process are dominant; at low velocities the electron cannot be considered as belonging to one proton in relation to its translation as a whole, especially at small R where the combinations $\phi_n^{g} \pm \phi_n^{u}$ do not localise the electron around one proton. However, at low velocities the influence of the translation phase factors is small and, furthermore, the presence of the variational parameter $f_n(R)$ will partially overcome these deficiencies by adopting small values for small R and v.

Schneiderman and Russek (1969), Thorson and Levy (1969) and Taulbjerg *et al* (1975) assume a phase factor $f(\boldsymbol{r}, R)$, the same for all channels; its functional form is determined so that it satisfies the correct boundary conditions for $R = 0$ and ∞. Since these phase factors are the same for all orbitals they cannot produce the specific time evolution of the electron density in each channel.

Sethu-Raman *et al* (1973) studied ionisation in low energy proton–hydrogen collisions using a phase factor for each molecular orbital, and fixed their form by requiring the coupling of each state with the continuum to be a minimum. These phase factors, instead of describing the electron density flux set up by the nuclear motion, are

used to modify the bound-state expansion so as to incorporate part of the continuum in it.

Riley and Green (1971) proposed the optimisation of phase factors using the Euler–Lagrange variational method for Schrödinger's equation. Two forms of wavefunction were discussed: employing a truncated expansion in a molecular or atomic basis, where each term goes to an atomic orbital centred in one of the nuclei at large R, they either used a unique phase factor or added a phase factor to each state of the expansion. Simultaneously, Ponce (1971) carried out the optimisation of the phase factors for the three states of H_2^+ of interest in low energy collisions; the use of a linear combination of atomic orbitals as an approximation to those states limits the validity of the results obtained to 'not-too-small' internuclear distances.

We will consider a molecular expansion, accompanying each state with a phase factor; these will be optimized separately using Euler–Lagrange equations in each channel; in this way we will obtain the best phase factors when transitions between channels are negligible. The basis so obtained will include the electron density flux generated by the nuclear motion. These phase factors will be explicitly calculated for the three lowest states of H_2^+, and applied to low energy charge-transfer and excitation processes.

2. Optimisation of phase factors

Our task is to follow the evolution of one electron in the time-varying potential created by two protons moving along classical trajectories with known velocities

$$\left(H_{el}(\boldsymbol{r}, t) - i\frac{\partial}{\partial t}\right)\Psi(\boldsymbol{r}, t) = 0 \tag{1}$$

$$H_{el}(\boldsymbol{r}, t) = -\tfrac{1}{2}\nabla_r^2 + V(\boldsymbol{r}, t) \qquad V(\boldsymbol{r}, t) = -\frac{1}{|\boldsymbol{r} - \frac{1}{2}\boldsymbol{R}|} - \frac{1}{|\boldsymbol{r} + \frac{1}{2}\boldsymbol{R}|} \tag{2}$$

(atomic units will be used). We propose the following truncated expansion for the wavefunction

$$\Psi(\boldsymbol{r}, t) = \sum_{n=1}^{N} c_n(t)\phi_n(\boldsymbol{r}, t)\, e^{if_n(\boldsymbol{r}, t)} \tag{3}$$

where the $\phi_n(\boldsymbol{r}, t)$ are real molecular eigenstates

$$(H_{el}(\boldsymbol{r}, t) - \epsilon_n(t))\phi_n(\boldsymbol{r}, t) = 0 \tag{4}$$

and $c_n(t)$ and $f_n(\boldsymbol{r}, t)$ are unknown functions to be determined by optimising $\Psi(\boldsymbol{r}, t)$ as an approximate solution of (1). The Euler–Lagrange equations are obtained by requiring that the functional

$$I = \int_{-\infty}^{\infty} dt \int d^3r\, \Psi^*\left(H_{el} - i\frac{\partial}{\partial t}\right)\Psi \tag{5}$$

be stationary with respect to arbitrary variations in those functions (Sil 1960, Cheshire 1968, McCarroll *et al* 1970). If $f_n(\boldsymbol{r}, t)$ is taken as a general real function of t and some

of the components of $\boldsymbol{r}$ in a certain reference frame, symbolised by $x_1, x_2, \ldots, x_p$ ($p \leqslant 3$), we get

$$\int \mathrm{d}^3 r\, \phi_j\, \mathrm{e}^{-\mathrm{i}f_j}\left(H_{\mathrm{el}} - \mathrm{i}\frac{\partial}{\partial t}\right)\Psi = 0 \tag{6a}$$

and the imaginary part of

$$\int \mathrm{d}x_{p+1} \ldots \mathrm{d}x_3\, c_j^*\, \phi_j\, \mathrm{e}^{-\mathrm{i}f_j}\left(H_{\mathrm{el}} - \mathrm{i}\frac{\partial}{\partial t}\right)\Psi = 0. \tag{6b}$$

They can be written

$$\sum_n \int \mathrm{d}^3 r\, \phi_j\, \mathrm{e}^{-\mathrm{i}(f_j - f_n)}\left[H_{\mathrm{el}} + \frac{1}{2}(\boldsymbol{\nabla}_r f_n)^2 + \frac{\partial f_n}{\partial t} - \mathrm{i}\left((\boldsymbol{\nabla}_r f_n)\boldsymbol{\nabla}_r + \frac{1}{2}\nabla_r^2 f_n + \frac{\partial}{\partial t}\right)\right] c_n \phi_n = 0 \tag{7a}$$

$$\sum_n \int \mathrm{d}x_{p+1} \ldots \mathrm{d}x_3 |c_j|\phi_j \left[\frac{\cos(f_n' - f_j')}{2|c_n|\phi_n}\left(\boldsymbol{\nabla}_r(\boldsymbol{\nabla}_r f_n) + \frac{\partial}{\partial t}\right)|c_n|^2 \phi_n^2 - \sin(f_n' - f_j')\left(H_{\mathrm{el}} + \frac{1}{2}(\boldsymbol{\nabla}_r f_n)^2 + \frac{\partial f_n'}{\partial t}\right)|c_n|\phi_n\right] = 0 \tag{7b}$$

where

$$c_n(t) = |c_n(t)|\, \mathrm{e}^{\mathrm{i}\delta_n(t)} \qquad f_n'(\boldsymbol{r}, t) = f_n(\boldsymbol{r}, t) + \delta_n(t).$$

Since we are certainly not in a position to solve the set of coupled integro-differential equations in f_j and c_j (7), some simplifications are needed: the phases f_j are coupled because they take into account the transition rates between channels, represented by the time dependence of the amplitudes c_j. We will neglect these transitions for the optimisation of f_j, so that equations (7*b*) may be replaced by

$$\int \mathrm{d}x_{p+1} \ldots \mathrm{d}x_3 \left(\boldsymbol{\nabla}_r(\boldsymbol{\nabla}_r f_j) + \frac{\partial}{\partial t}\right)\phi_j^2 = 0. \tag{8}$$

For a general $f_j(\boldsymbol{r}, t)$ ($p = 3$), (8) represents the continuity equation for the *adiabatic* evolution of ϕ_j. In this way we are optimising the basis used for the expansion of Ψ in the regime of small collision velocities.

Let us analyse the main features of the electronic flux set up by the nuclear motion: *the change of the internuclear distance* R produces a general velocity field, and it can be assumed that its most important component is along $\boldsymbol{R}$, taken as the $\hat{e}_z$ direction in a coordinate system rotating with $\boldsymbol{R}$. For large R this velocity field is exactly along $\boldsymbol{R}$, while at small R we can expect the appearance of a component v_x normal to $\boldsymbol{R}$ and in the plane of the nuclear motion. This velocity field originates from the shrinking electron distribution in all directions which forms the united-atoms orbital at $R = 0$. We will assume that velocity components normal to the plane of nuclear motion are negligible. Then $\mathring{R}$ originates a field

$$\mathring{R}(v_x(\boldsymbol{r}, t)\hat{e}_x + v_z(\boldsymbol{r}, t)\hat{e}_z). \tag{9}$$

The rotational motion of $\boldsymbol{R}$ represented by the angular velocity $\mathring{\theta}$ produces a velocity field whose $\boldsymbol{r}$ dependence is exactly known

$$\mathring{\theta}(z\hat{e}_x - x\hat{e}_z). \tag{10}$$

Since the continuity equation for the electronic density is

$$\nabla_r(v(r,t)\phi^2(r,R))+\frac{\partial}{\partial t}\phi^2(r,R)=0 \tag{11}$$

by comparing it with (8) we conclude that a form for the phase factors must be proposed such that its gradient approximates the velocity fields of (9) and (10).

It is reasonable to assume that the electron flux set up by the radial motion acts along $\boldsymbol{R}$ and depends on the electron coordinate z along $\boldsymbol{R}$; this behaviour can be represented by a phase factor

$$g(z,t). \tag{12}$$

We will add a phase

$$h(x,t) \tag{13}$$

that produces a velocity along $\hat{e}_x$ and is dependent only on x; this phase gives an idea of the importance of the electron flux normal to $\boldsymbol{R}$.

The rotation $\mathring{\theta}$ produces a flux that cannot be represented by a gradient, so we must settle for a partial description of (10): for the electron density around the internuclear line (that is *all* the density for large R), the velocity field set up by the rotation is $z\mathring{\theta}\hat{e}_x$. We then propose a phase

$$w(t)xz \tag{14}$$

where w is a general function of t, which reproduces the velocity field (10) for the density along the internuclear line, and also gives the velocity field if the density is concentrated in a plane normal to R: $-x\mathring{\theta}\hat{e}_z$. The variational function $w(t)$ will consider the importance of these two regions for each value of R, and will produce a compromised phase factor.

The phase factor to be optimised for each molecular state then has the form

$$f(r,t)=g(z,t)+h(x,t)+w(t)xz \tag{15}$$

and can satisfy the asymptotic condition

$$\nabla_r f(r,t)\to\tfrac{1}{2}vz/r \qquad \text{when } R\to\infty. \tag{16}$$

We may compare our procedure with the formalism of Bates and McCarroll improved by Crothers and Hughes. They assumed a velocity field along the nuclear trajectories, where each proton influences the electron density represented by the combinations $\frac{1}{2}(\phi_n^g\pm\phi_n^u)$, and the phase factors that accompany these terms are $\pm f_n(R)(\mathring{R}z+R\mathring{\theta}x)$ respectively; these phase factors are a special case of the class of functions (15). The main difference between this approach and ours is that we do not explicitly separate the regions of influence of each proton on the electron density flux.

Remembering that x, y, z are rotating coordinates, the Euler–Lagrange equations (8) for g, h and w are

$$\frac{\partial}{\partial z}\int dx\,dy\,[g_z+x(\mathring{\theta}+w)]\phi^2+\frac{\partial}{\partial t}\int dx\,dy\,\phi^2=0 \tag{17a}$$

$$\frac{\partial}{\partial x}\int dy\,dz\,[h_x+z(w-\mathring{\theta})]\phi^2+\frac{\partial}{\partial t}\int dy\,dz\,\phi^2=0 \tag{17b}$$

$$\int d^3r[xg_z + zh_x + w(x^2+z^2) + \dot{\theta}(x^2-z^2)]\phi^2 - \frac{\partial}{\partial t}\int d^3r\, xz\phi^2 = 0 \qquad (17c)$$

where $g_z = \partial g/\partial z$, etc, and the time derivatives are carried out keeping the rotating coordinates x, y, z constant. After cancelling asymmetric terms in x and z, and integrating (17a, b) in z and x respectively, we obtain

$$g_z(z,t) = -\dot{R}\int_0^z dz' \int dx\, dy \frac{\partial}{\partial R}\phi^2(x,y,z',R)\left(\int dx\, dy\, \phi^2(x,y,z,R)\right)^{-1} \qquad (18a)$$

$$h_x(x,t) = -\dot{R}\int_0^x dx' \int dy\, dz \frac{\partial}{\partial R}\phi^2(x',y,z,R)\left(\int dy\, dz\, \phi^2(x,y,z,R)\right)^{-1} \qquad (18b)$$

$$w(t) = \dot{\theta}\int d^3r\,(z^2-x^2)\phi^2(x,y,z,R)\left(\int d^3r\,(z^2+x^2)\phi^2(x,y,z,R)\right)^{-1}. \qquad (18c)$$

The integrations in (18) have to be performed numerically. We will consider the three states of H_2^+ that are active during a collision at low energies: $1s\sigma_g$, $2p\sigma_u$ and $2p\pi_u$. Their exact wavefunctions are known but, since numerical integration already introduces a small error in the results, to ease the computational work we will use approximate forms with three variational parameters (Clark and Theal Stewart 1969, Arista and Ponce 1973). These functions reproduce binding energies within one part in 10^6, and coupling matrix elements within one part in 10^3.

3. Results

Figure 1 shows $g_z(z,t)$ for the three states considered and selected values of R; g_z reproduces the velocity field along $\boldsymbol{R}$ caused by the radial motion.

We now relate the characteristics of these velocity distributions to the form of the electron densities and their dependence on R.

$1s\sigma_g$. This is the only bound state of H_2^+, the binding being produced by an accumulated electron charge between the protons. This behaviour persists up to $R = 3$ au; from then on the electron velocity is higher than $\dot{R}/2$ around the protons, where the density is appreciable, and a symmetrical density around each nucleus tends to be restored.

$2p\sigma_u$. This is antisymmetric with nodal plane $z = 0$. For small R the electron density is very small in the internuclear region. When the protons move apart the density flux goes first in the opposite direction (negative velocity in figure 1(b)), and later remains slower than $\dot{R}/2$: the excess of extranuclear charge diminishes continuously up to $R = \infty$.

$2p\pi_u$. This is also antisymmetric, with nodal plane $x = 0$. This allows a build-up of internuclear charge outside the plane which is not strong enough to produce a bound state. As with $1s\sigma_g$ we will have a delay of electron flux with respect to the protons; though this effect will be less marked now because the electron density extends over a greater volume, and consequently larger changes in R are needed to produce the same effects as for $1s\sigma_g$.

Figure 2 presents w as a function of R. This parameter is related to the rotation of the molecular orbitals with angular velocity $\dot{\theta}$. At small R the state $1s\sigma_g$ goes to a spherically symmetric orbital 1s. The rotation of R will not affect this orbital and so

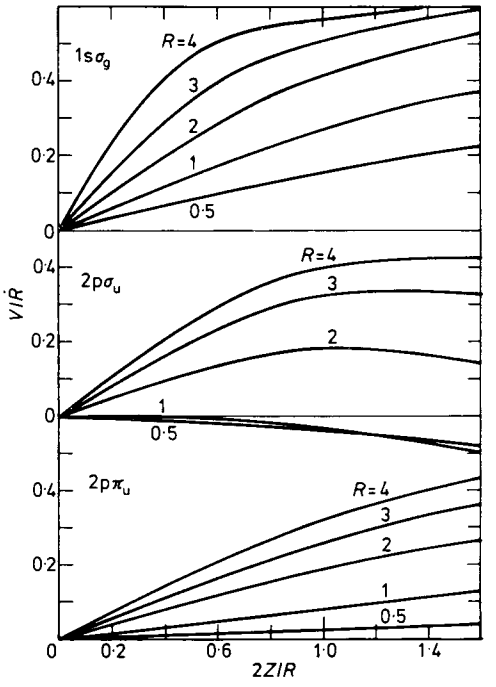

Figure 1. Field of velocities $v = g_z(z, t)$ in direction $\boldsymbol{R}$ produced by the radial motion $\mathring{R}$ of the protons, for various internuclear distances R and as a function of the electronic coordinate z measured in units of $R/2$. $2z/R = 1$ defines the plane normal to $\boldsymbol{R}$ containing one of the protons, while $2z/R = 0$ is the plane through the midpoint between the protons.

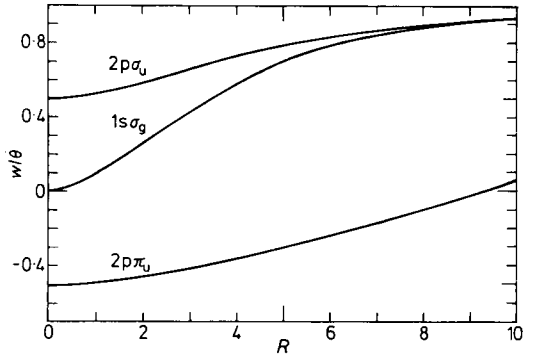

Figure 2. Variational parameter $w(t)$ in units of the nuclear rotation $\mathring{\theta}$, as a function of the internuclear distance R.

$w \to 0$ as $R \to 0$. $2p\sigma_u$ goes to the orbital $2p_0$ whose charge density is distributed along $\boldsymbol{R}$; then the important component of the rotational velocity field (10) is $\mathring{\theta} z \hat{e}_x$, and $w(R = 0)$ is positive. When $R \to 0$ the state $2p\pi_u$ results from a rotation of $2p\sigma_u$ by $\pi/2$, then the predominant velocity in (10) is $-\mathring{\theta} x \hat{e}_z$ and we get the same value for $w(R = 0)$ with a negative sign.

For large R and for all states, $g_z(z, t) \to \mathring{R}/2$ and $w(t) \to \mathring{\theta}$, thus reproducing the correct asymptotic velocity of translation $\mathring{R}\hat{e}_z/2 + \mathring{\theta} z \hat{e}_x$ (for large R the electronic density is concentrated around the protons and we can replace z by $R/2$).

The phase factor $h(x, t)$ produces a field of velocities normal to $\boldsymbol{R}$ generated by the radial velocity $\mathring{R}$. The asymptotic value of the velocity $h_x(x, t)\hat{e}_x$ is zero, and the results obtained show that it remains small at finite R, being a factor of three smaller than the corresponding velocity $g_z(z, t)\hat{e}_z$ for the states considered. These velocities are only comparable for $2p\sigma_u$ and $R < 1$ but then both are small; therefore, we will eliminate the phase factor $h(x, t)$ from our study of the collision, since the remaining phases in (15) reproduce the asymptotic behaviour and describe the important part of the electron density flux generated by the nuclear motion.

The results presented in figures 1 and 2 show that the phase factors differ considerably for the three states studied, so the use of a unique phase factor for the wavefunction (3) (Schneiderman and Russek 1969, Taulbjerg *et al* 1975, Crothers and Hughes 1978) represents an important simplification in the description of the collision process. In agreement with previous works (Ponce 1971, Crothers and Hughes 1978), it is seen that the phase factors for $R < 2$ are considerably smaller than the plane-wave factors proposed by Bates and McCarroll (1958), so we can expect that their influence on the collision will also be smaller. Two interesting features of these optimised phases are the small and even negative velocity field $2p\sigma_u$ produced by the radial motion $\mathring{R}$, and the change in sign of the optimised rotation velocity $w(t)$ for $2p\pi_u$, that goes from $\mathring{\theta}$ at large R to $-\mathring{\theta}/2$ at $R = 0$; this behaviour is the main difference between our results and the phase factors suggested by Sethu-Raman *et al* (1973).

4. Application to $H^+ + H(1s)$ collisions

We will apply the wavefunction (3) with the optimised phase factors (15) to the study of proton–hydrogen-atom collisions; for low energy processes ($v \ll 1$) the active states are $1s\sigma_g(\equiv 0)$, $2p\sigma_u(\equiv 1)$ coming from the initial 1s orbital, and $2p\pi_u(\equiv 2)$ populated through the $2p\sigma_u$–$2p\pi_u$ rotational coupling. The impact-parameter approximation with straight-line trajectories will be used to describe the nuclear motion.

From (18) we see that the parity of the molecular states is conserved when accompanied by the phase factors (15). The orthogonality between σ and π orbitals is not conserved, even after removing the phase $h(x, t)$ as in the following. The system of coupled equations (7*a*) for the amplitudes is reduced to

$$\sum_n \left(i\frac{dc_n}{dt} S_{kn} - c_n M_{kn} \right) = 0 \tag{19}$$

where

$$S_{kn} = \langle \phi_k | \, e^{i(f_n - f_k)} | \phi_n \rangle \tag{20a}$$

$$M_{kn} = \left\langle \phi_k \middle| \, e^{i(f_n - f_k)} \left[\epsilon_n(R) + \frac{1}{2}(\nabla_r f_n)^2 - i\left(\nabla_r f_n \nabla_r + \frac{1}{2}\nabla_r^2 f_n + \frac{\partial}{\partial t} \right) \right] \middle| \phi_n \right\rangle \qquad k \neq n$$
$$+ \frac{\partial f_m}{\partial t} \tag{20b}$$

$$M_{kk} = \left\langle \phi_k \middle| \epsilon_k(R) + \frac{1}{2}(\nabla_r f_k)^2 + \frac{\partial f_k}{\partial t} \middle| \phi_k \right\rangle. \tag{20c}$$

The couplings (20*b*) depend on $\mathring{R}$ and $\mathring{\theta}$ through the phase factors, so their dependence on impact parameter and velocity is not simple. To ease the computations we expand (20*b*) in powers of v and conserve up to and including quadratic terms; the contributions come from terms in $\mathring{R}$, $\mathring{\theta}$, $\mathring{R}^2$, $\mathring{R}\mathring{\theta}$, $\mathring{\mathring{R}}$, $\mathring{\mathring{\theta}}$ with coefficients that depend only on R. It

can be seen that the parameters $w(t)$ produce terms $\mathring{\theta}$ linear in v, while $g(z, t)$ gives rise to terms $\mathring{\mathring{R}}$ of the order of v^2; this indicates that the phase factors associated with the nuclear rotation $\mathring{\theta}$ are more important for the transition than the phases coming from the radial motion $\mathring{R}$.

Numerical calculations of the coupled system (19) were carried out using the computer programs of Gaussorgues *et al* (1975) adapted to our problem. The probability of excitation to the $2p_1$ level in either target or projectile $|c_2(\infty)|^2$ is presented in figure 3 for several impact energies, and compared with the results without phase factors, and with plane-wave phases used by Bates and Williams (1964) (these authors conserve up to linear terms in v in the rotational coupling). We observe that the contribution of our phase factors is small, less than can be expected from the magnitude of the impact velocities considered. This is due to the fact that the optimised phase factors are small for $R < 1$, which is the region where the coupling M_{12} is important. Bates and Williams use combinations of molecular orbitals that localise the electron around a proton at large R, and assume that each term moves with the same velocity of the proton for all values of R; this produces an overestimation of the effect of the phase factors on the excitation probability, as is shown in figure 3.

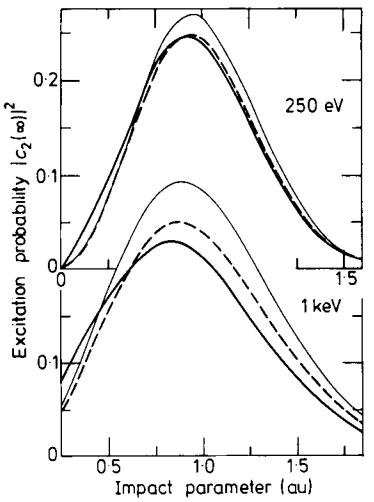

Figure 3. Probability of excitation to the $2p_1$ state in either target or projectile as a function of the impact parameter for 0·25 and 1 keV incident proton energy, and assuming straight-line nuclear trajectories: ——, present results with optimised phase factors; – – –, present results without phase factors; ——, results of Bates and Williams (1964), with plane-wave phase factors.

We also obtain the total probability for charge exchange as a function of the scattering angle θ:

$$p^{ex}(\theta) = (\sigma^{ex}_{1s}(\theta) + \sigma^{ex}_{2p_1}(\theta))/\sigma^{tot}(\theta) \tag{21}$$

where σ^{ex}_{1s} and $\sigma^{ex}_{2p_1}$ are the differential cross sections for charge transfer to the 1s and $2p_1$ states, and $\sigma^{tot}(\theta)$ is the sum of all the differential cross sections for direct and exchange scattering into the angle θ. These cross sections are calculated in the eikonal approximation, formulated in the field of atomic collisions by McCarroll and Salin

(1968), Wilets and Wallace (1968) and Chen and Watson (1968); in this approach the relation between the impact parameter ρ and angle θ is treated semiclassically, and our results will be valid for collision energies of a few tens of electron volts, while the usual classical description of the nuclear motion and corresponding one-to-one relation between ρ and θ becomes valid at much higher energies. In the eikonal approximation $\sigma(\theta)$ is obtained from the integration over impact parameters of the amplitudes c_n multiplied by Bessel functions of the argument $2\mu v\,\rho \sin \theta/2$, where μ is the reduced mass of the collision system. We use the numerical method proposed by Piacentini and Salin (1977) to perform this quadrature, and the results obtained for several collision energies are shown in figure 4. We see that when phase factors are considered there is a shift in the phase of the oscillations with the angle θ that increases with collision energy.

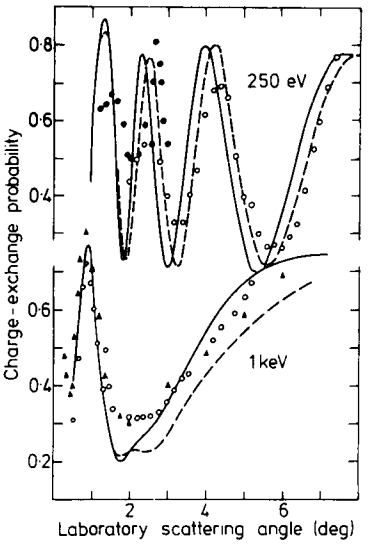

Figure 4. Probability of capture to the 1s or $2p_1$ state of the projectile by protons of 0·25 and 1 keV energy, as a function of the scattering angle: ——, present results with optimised phase factors; – – –, present results without phase factors. Experimental points ▲, ● are taken from Helbig and Everhart (1965); while ○ are taken from Houver *et al* (1974).

The capture results of Bates and Williams do not depend on their plane-wave factors except through the amplitude $c_2(\infty)$; then they are very similar to our results without phase factors in the frame of the eikonal approximation. The discrepancy between the results with and without phase factors is very small for low collision energies or small scattering angles. This difference increases with E and θ, but we should be careful not to apply our formalism outside its region of validity, since the use of rotating orbitals and the associated translation factors is only justified for small rotation velocities (Schneiderman and Russek 1969) and to keep $\mathring{\theta}$ small it is necessary to consider impact parameters larger than the numerical value of the collision velocity: $\mathring{\theta} < v/\rho < 1$.

5. Conclusions

The usual expansion in molecular orbitals for the description of low energy atomic collisions has been modified by adding a phase factor to each state considered. The

phases have been separately optimised so that they take into account the electron flux created by the nuclear motion in each channel. The results obtained show the following.

(*a*) The phase factors are strongly dependent on the molecular orbital (figures 1 and 2), so it may be incorrect to use a unique factor for all the states of the basis.

(*b*) The phases are smaller than the plane-wave phases of Bates and McCarroll at the internuclear distances of interest for inelastic collisions, and so the effect of the optimised phase factors on inelastic collisions is appreciably smaller than that obtained by Bates and Williams with plane-wave phases (figure 3).

(*c*) The optimised phase factors introduce an additional phase in the oscillations of the probability of charge exchange that increases with the collision energy (figure 4).

We conclude that the use of translational factors that describe the electron density flux correctly does not produce an appreciable change in the results obtained without those factors, at least for low energy proton–hydrogen-atom collisions. If the effect of the phase factors on the results is required, then it may be necessary to optimise them separately for each state, and to consider the electronic density flux generated by both the radial and rotational motion of the internuclear coordinate.

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