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Wave operators for atomic photo-ionisation

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Abstract. The time development of a system consisting of an atom in an external electromagnetic field with fixed propagation direction is studied (vector potential $\boldsymbol{A}(\boldsymbol{x}, t) = \boldsymbol{A}(x_3 - ct)$). It is shown that the Møller wave-operators, relevant for photo-ionisation, exist, provided the components $A_\sigma(u)$ of $\boldsymbol{A}$ decay as $|u|^{-1-\varepsilon}$, $\varepsilon > 0$, for large argument u. Since $\boldsymbol{A}(\boldsymbol{x}, t)$ is not necessarily spatially homogeneous, the above results can serve as a starting point for an investigation of field-gradient effects on photo-ionisation processes.

1. Introduction

In semiclassical theories of multiphoton ionisation of atoms the field that causes the ionisation process enters into the Hamiltonian through the vector potential $\boldsymbol{A}(\boldsymbol{x}, t)$. The simplest way to proceed is then to neglect the $\boldsymbol{x}$ dependence of $\boldsymbol{A}$ (the so-called long-wavelength approximation). In addition the field is often assumed to be monochromatic. In practice experiments are performed with fields produced by pulsed lasers so that we are dealing with radiation fields which are localised in both space and time. In view of the very intense laser pulses that can nowadays be obtained (10^{15} to 10^{16} Watt/cm^2) it becomes of interest to know what effects the field gradients can have on phenomena such as multiphoton ionisation of atoms (Boreham and Hughes 1981, Agostini *et al* 1981).

In the present work we study some aspects of a model where an atom is influenced by an external field with a fixed propagation direction. The vector potential is given by

$$\boldsymbol{A}(\boldsymbol{x}, t) = \{A_1(x_3 - ct), A_2(x_3 - ct), 0\}. \tag{1.1}$$

Thus $\boldsymbol{A}(\boldsymbol{x}, t)$ is divergence free and propagates in the $\hat{x}_3$ direction. In this way pulses can be described that are localised in this direction and in time but are still of infinite extent in the two other space directions. This still leaves something to be desired but, on the other hand, the advantage of the present model is that the explicit time-dependence of the Hamiltonian can be transformed away.

We neglect spin effects in our description of the atom. The Hamiltonian is then given by (in atomic units)

$$\begin{aligned} H(t) &= \sum_{j=0}^{N} (2m_j)^{-1}[\boldsymbol{p}_j - e_j\boldsymbol{A}(x_{j3} - \alpha^{-1}t)]^2 + \sum_{0 \le j < h \le N} e_j e_h |\boldsymbol{x}_j - \boldsymbol{x}_h|^{-1} \\ &= \sum_{j=0}^{N} (2m_j)^{-1}[\boldsymbol{p}_j - e_j\boldsymbol{A}(x_{j3} - \alpha^{-1}t)]^2 + V. \end{aligned} \tag{1.2}$$

Here coordinates are measured in units a_0 (the Bohr radius), time in units $ma_0^2/\hbar$, charges in units e (the absolute value of the electronic charge), masses in units m (the electronic mass). α is the fine-structure constant. Particle 0 is the nucleus with mass m_0 and charge $e_0 = N$ whereas particles 1 to N are the electrons with mass $m_j = 1$ and charge $e_j = -1$.

General results exist concerning the self-adjointness of $H(t)$ for some fixed $t \in \mathbb{R}$ (Jörgens and Weidmann 1970, Schechter 1971). Here we shall assume that the two non-zero components $A_\sigma(u)$, $\sigma = 1, 2$, of the vector potential are essentially bounded measurable functions of their argument, i.e. $A_\sigma(u) \in L^\infty(\mathbb{R}, \mathrm{d}u)$. Thus $A_\sigma(x_{j3} - \alpha^{-1}t)$ defines a bounded multiplication operator acting in the Hilbert space $\mathscr{H} = L^2(\mathbb{R}^{3(N+1)}, \mathrm{d}\boldsymbol{x}_0 \ldots \mathrm{d}\boldsymbol{x}_N)$. Then $H(t)$ is self-adjoint with domain $\mathscr{D} = \mathscr{D}(T)$, where

$$T = \sum_{j=0}^{N} (2m_j)^{-1} \boldsymbol{p}_j^2 \tag{1.3}$$

is the total kinetic energy operator. In particular $\mathscr{D}$ does not depend on $t \in \mathbb{R}$. We note further that all contributions to $H(t) - T$ are relatively T-bounded with zero relative bound.

General methods exist (Kato 1953, 1970, Yosida 1968) to determine whether or not $H(t)$ defines a unitary time-evolution operator, i.e. a solution of the equation

$$\partial_t U(t, t_0) = -\mathrm{i}H(t)U(t, t_0) \tag{1.4}$$

subject to the initial condition $U(t_0, t_0) = 1$. One such method was employed by Combe *et al* (1975) who considered a hydrogen atom in the Born–Oppenheimer approximation. In our case, however, there exists a simple time-dependent unitary transformation which leads to a time-independent Hamiltonian so that the existence of $U(t, t_0)$ becomes a straightforward matter.

In § 2 we prove the existence of $U(t, t_0)$ and we define the Møller wave-operators relevant for photo-ionisation. In § 3 we demonstrate the existence of the latter. Our case differs from the one considered by Combe *et al* (1975) since these authors assumed the vector potential to be independent of the coordinates. We, on the other hand, assume $\boldsymbol{A}(x_3 - \alpha^{-1}t)$ to vanish for large values of its argument and this was not assumed by the above-mentioned authors. The case we consider is somewhat closer to the actual experimental situation where the ionisation products are measured in a space–time region where the field vanishes.

In § 4 we discusss briefly two special cases. The first is that of an infinitely heavy nucleus (Born–Oppenheimer approximation) and the second that of a spatially homogeneous field. A discussion section concludes the present work. In a subsequent paper we shall discuss the connection between the scattering operator, defined in terms of the wave operators, whose existence is proven in the present work, and the physical quantities that are measured in an actual experiment.

2. Time evolution

In this section we show the existence of $U(t, t_0)$ and that it possesses the usual properties of a time-evolution operator, i.e. $U(t, t_0)$ is strongly continuous in t, it maps $\mathscr{D}$ into itself, $U(t, t_1)U(t_1, t_0) = U(t, t_0)$, $U(t, t_0)^* = U(t, t_0)^{-1} = U(t_0, t)$. In order to obtain these results we make use of a translation in coordinate space. Thus let

$$P = \sum_{i=0}^{N} p_i \tag{2.1}$$

be the total momentum operator. Since its components are self-adjoint operators the family

$$\{Y(t) = \exp(-i\alpha^{-1}P_3 t) \mid t \in \mathbb{R}\} \tag{2.2}$$

constitutes a strongly continuous group of unitary operators. In Fourier space T is a multiplication operator and $Y(t)$ a multiplication by a phase factor which leaves $\tilde{\mathscr{D}}$, the image of $\mathscr{D}$ under Fourier transformation, invariant. Consequently $Y(t)$ leaves $\mathscr{D}$ invariant. Momentum variables are left invariant under the transformation $p_j \to Y(t)p_jY(t)^{-1}$ whereas coordinates are translated according to

$$Y(t)x_jY(t)^{-1} = x_j - \alpha^{-1}te_3, \tag{2.3}$$

e_σ, $\sigma = 1, 2, 3$, being the unit vector along the $\hat{x}_\sigma$ axis. Let $M = \Sigma_{j=0}^{N} m_j$ be the total mass and

$$X = M^{-1} \sum_{j=0}^{N} m_j x_j \tag{2.4}$$

be the centre-of-mass (CM) position vector. Since its components are self-adjoint operators

$$Z = \exp(iM\alpha^{-1}X_3) = \exp\left(i\alpha^{-1} \sum_{j=0}^{N} m_j x_{j3}\right) \tag{2.5}$$

is a unitary operator. Since Z acts as a phase factor on elements of $\mathscr{H}$ it maps $\mathscr{D}$ onto itself. The transformation $x_j \to Zx_jZ^{-1}$ leaves x_j invariant but momenta undergo a translation

$$Zp_jZ^{-1} = p_j - m_j\alpha^{-1}e_3. \tag{2.6}$$

Let

$$\tilde{H} \equiv H(t=0) = \sum_{j=0}^{N} (2m_j)^{-1}[p_j - e_jA(x_{j3})]^2 + V. \tag{2.7}$$

Then

$$H(t) = Y(t)\tilde{H}Y(t)^{-1}, \tag{2.8}$$

in the sense that the left- and right-hand sides of (2.8) give the same result when acting upon an element $\psi \in \mathscr{D}$. This follows from the fact that momenta are left invariant under the transformation on the right in (2.8) and coordinates are shifted according to (2.3). Since V only depends on the differences of position vectors it is left invariant (V commutes with the total momentum vector). We note further that $H(t)$ and $\tilde{H}$ have the same domain $\mathscr{D}$ and $Y(t)$ maps $\mathscr{D}$ onto itself. Let now

$$\hat{H} = \tilde{H} - \alpha^{-1}P_3. \tag{2.9}$$

$\hat{H}$ with domain $\mathscr{D}$ is self-adjoint since P_3 is T-bounded with zero relative bound (note that $\mathscr{D}(P_3)$, the domain of P_3, contains $\mathscr{D}$). Thus

$$\{\hat{U}(t) = \exp(-i\hat{H}t) \mid t \in \mathbb{R}\} \tag{2.10}$$

defines a strongly continuous group of unitary operators. Next we define a family of unitary operators according to

$$\{U(t) = Y(t)\hat{U}(t) \mid t \in \mathbb{R}\}. \tag{2.11}$$

For $\psi \in \mathscr{D}$, $\hat{U}(t)\psi \in \mathscr{D}$ and $\hat{H}\hat{U}(t)\psi = \hat{U}(t)\hat{H}\psi$ (Kato 1966, p 481). Similarly $P_3 Y(t)\psi = Y(t)P_3\psi$ for $\psi \in \mathscr{D}(P_3)$. Since $Y(t)$ maps $\mathscr{D}$ onto itself we also have $U(t)\psi \in \mathscr{D}$. Now, using the inclusion relation $\mathscr{D}(P_3) \supset \mathscr{D}$, we have for each $\psi \in \mathscr{D}$:

$$\begin{aligned} \partial_t U(t)\psi &= \partial_t Y(t)\hat{U}(t)\psi = -\mathrm{i}\alpha^{-1} P_3 Y(t)\hat{U}(t)\psi - \mathrm{i}Y(t)\hat{H}\hat{U}(t)\psi \\ &= -\mathrm{i}\alpha^{-1}[P_3 Y(t) - Y(t)P_3]\hat{U}(t)\psi - \mathrm{i}Y(t)\hat{H}Y^{-1}(t)U(t)\psi \\ &= -\mathrm{i}H(t)U(t)\psi. \end{aligned} \tag{2.12}$$

It follows that

$$U(t, t_0) = U(t)U(t_0)^{-1} = Y(t)\exp[-\mathrm{i}\hat{H}(t - t_0)]Y(t_0)^{-1} \tag{2.13}$$

is a solution of (1.4) and has the properties mentioned in the introduction of this section. Its uniqueness is clear from the following considerations: let $\psi(t) \in \mathscr{D}$ be a solution of

$$\partial_t \psi(t) = -\mathrm{i}H(t)\psi(t) \tag{2.14}$$

subject to the initial condition $\psi(0) = \psi$. Then

$$\partial_t Y^{-1}(t)\psi(t) = -\mathrm{i}\hat{H}Y^{-1}(t)\psi(t) \tag{2.15}$$

but this equation has the unique solution

$$Y^{-1}(t)\psi(t) = \exp(-\mathrm{i}\hat{H}t)Y^{-1}(t=0)\psi(t=0) = \exp(-\mathrm{i}\hat{H}t)\psi,$$

i.e. $\psi(t) = U(t)\psi$. We can rewrite (2.9) in the form

$$\begin{aligned} \hat{H} &= \sum_{j=0}^{N} (2m_j)^{-1}[\boldsymbol{p}_j - e_j \boldsymbol{A}(x_{j3}) - m_j\alpha^{-1}\boldsymbol{e}_3]^2 + V - M/(2\alpha^2) \\ &= Z\tilde{H}Z^{-1} - M/(2\alpha^2). \end{aligned} \tag{2.16}$$

Accordingly we have

$$\hat{U}(t) = \exp[\mathrm{i}Mt/(2\alpha^2)]Z\tilde{U}(t)Z^{-1}, \tag{2.17}$$

$$U(t) = \exp[\mathrm{i}Mt/(2\alpha^2)]Y(t)Z\tilde{U}(t)Z^{-1}, \tag{2.18}$$

where

$$U(t) = \exp(-\mathrm{i}\tilde{H}t). \tag{2.19}$$

We now consider the case that an atom is ionised due to the action of the electromagnetic field. Under the assumption that $A_\sigma(u)$ vanishes for large values of its argument we can encounter the situation that, asymptotically, for $t \to -\infty$, the atom is freely moving and in an eigenstate of its internal motion (the ground state, in practice). Then ionisation takes place and, asymptotically for $t \to +\infty$, we have a freely moving electron and positive ion. Of course the possibility exists that more electrons are stripped off the ion, but this process is usually not studied experimentally.

Thus in the entrance channel the asymptotic motion is governed by the Hamiltonian

$$H^{\mathrm{in}} = \sum_{j=0}^{N} (2m_j)^{-1}\boldsymbol{p}_j^2 + V = T^{\mathrm{CM}} + H^{\mathrm{at}} \tag{2.20}$$

where $T^{CM}=(2M)^{-1}\boldsymbol{P}^2$ and H^{at} are the Hamiltonians associated with the centre-of-mass motion and the internal atomic motion, respectively. In the exit channel we are dealing with a freely moving electron and positive ion. At this stage the Pauli principle must be taken into account (H^{in} is invariant under interchange of the electrons so that antisymmetry is preserved under the corresponding time evolution). It is sufficient, however, to consider the case that a specific electron, say 1, is ionised, as will be discussed in a subsequent paper. The Hamiltonian associated with the outgoing channel then becomes

$$H^{out}=T^{CM}+T^1+H^{ion}, \tag{2.21}$$

where T^1 is the Hamiltonian associated with the relative motion of electron 1 with respect to the centre of mass of the ion consisting of the nucleus and electrons 2 to N. H^{ion} is the Hamiltonian associated with the internal motion of the ion. (The definitions of the various coordinates and momenta are given in the appendix.)

The asymptotic motion in the entrance channel is governed by

$$U^{in}(t)=\exp(-iH^{in}t) \tag{2.22}$$

and the Møller operators for this channel are the strong limits

$$\Omega_{\pm}^{in}=\operatorname*{s-lim}_{t\to\pm\infty}\Omega^{in}(t)=\operatorname*{s-lim}_{t\to\pm\infty}U^*(t)U^{in}(t)P^{in} \tag{2.23}$$

or, in terms of

$$\hat{U}^{in}(t)=\exp(-i\hat{H}^{in}t), \qquad \hat{H}^{in}=H^{in}-\alpha^{-1}P_3, \tag{2.24}$$

$$\Omega_{\pm}^{in}=\operatorname*{s-lim}_{t\to\pm\infty}\exp(i\hat{H}t)\exp(-i\hat{H}^{in}t)P^{in} \tag{2.25}$$

since P_3 and H^{in} commute.

Here $P^{in}=I^{CM}\otimes P^{at}$ where I^{CM} is the identity operator acting in $\mathscr{H}^{CM}$, the Hilbert space associated with the centre-of-mass motion, and P^{at} is the projector upon the atomic bound states (i.e. the closed linear span of the atomic eigenstates) in the Hilbert space $\mathscr{H}^{at}$, associated with the internal atomic motion.

In the outgoing channel we are dealing with charged particles. Thus we have to modify the asymptotic time evolution to take into account the long-range nature of the Coulomb force (Dollard 1964). Thus

$$U^{out}(t)=\exp(-iH^{out}t)U_c'(t), \tag{2.26}$$

where

$$U_c'(t)=\exp[i\ln(2|t|q_1^2/m_1)t/(q_1|t|)], \qquad t\neq 0. \tag{2.27}$$

Here $\boldsymbol{q}_1$ is the momentum operator associated with the relative motion of electron 1 with respect to the ionic centre of mass, $q_1=(\boldsymbol{q}_1^2)^{1/2}$ and m_1 is the corresponding reduced mass (thus $T_1=q_1^2/(2m_1)$, see the appendix for details). The wave operators for the outgoing channel are now defined as

$$\Omega_{\pm}^{out}=\operatorname*{s-lim}_{t\to\pm\infty}\Omega^{out}(t)=\operatorname*{s-lim}_{t\to\pm\infty}U^*(t)U^{out}(t)P^{out}$$

$$=\operatorname*{s-lim}_{t\to\pm\infty}\hat{U}^*(t)\hat{U}^{out}(t)P^{out}, \tag{2.28}$$

where

$$\hat{U}^{\rm out}(t) = \exp(-{\rm i}\hat{H}^{\rm out}t)U'_{\rm c}(t), \qquad \hat{H}^{\rm out} = H^{\rm out} - \alpha^{-1}P_3. \tag{2.29}$$

In (2.28), $P^{\rm out} = I^{\rm CM} \otimes I^1 \otimes P^{\rm ion}$, I^1 being the identity operator in $\mathscr{H}^1$, the Hilbert space associated with the relative electron–ion motion, $P^{\rm ion}$ is the projector upon the ionic eigenstates in $\mathscr{H}^{\rm ion}$, the Hilbert space associated with the internal motion of the ion.

A simple calculation shows that

$$\exp(-{\rm i}T^{\rm CM}t) = \exp[{\rm i}Mt/(2\alpha^2)]Y(t)Z\exp(-{\rm i}T^{\rm CM}t)Z^{-1} \tag{2.30}$$

and, since the remaining terms in $H^{\rm in}$, $H^{\rm out}$ and $U'_{\rm c}(t)$ do not depend on the CM variables, (2.30) holds with $\exp(-{\rm i}T^{\rm CM}t)$ replaced by $U^{\rm in}(t)$ and $U^{\rm out}(t)$, respectively. It follows that

$$\Omega^{\rm in}(t) = Z\tilde{\Omega}^{\rm in}(t)Z^{-1}, \qquad \Omega^{\rm out}(t) = Z\tilde{\Omega}^{\rm out}(t)Z^{-1}, \tag{2.31}$$

where

$$\tilde{\Omega}^{\rm in}(t) = \exp({\rm i}\tilde{H}t)U^{\rm in}(t)P^{\rm in}, \qquad \tilde{\Omega}^{\rm out}(t) = \exp({\rm i}\tilde{H}t)U^{\rm out}(t)P^{\rm out}. \tag{2.32}$$

Since Z is unitary it follows that the existence of $\Omega^{\rm in}_{\pm}$ and $\Omega^{\rm out}_{\pm}$ is equivalent to the existence of

$$\tilde{\Omega}^{\rm in}_{\pm} = \operatorname*{s-lim}_{t\to\pm\infty} \tilde{\Omega}^{\rm in}(t) \tag{2.33}$$

and

$$\tilde{\Omega}^{\rm out}_{\pm} = \operatorname*{s-lim}_{t\to\pm\infty} \tilde{\Omega}^{\rm out}(t), \tag{2.34}$$

respectively.

In § 3 we outline an existence proof for the $\tilde{\Omega}$ operators. We find that they exist provided

$$\sup_{w\in\mathbb{R}} |w|^{\kappa} A^2_{\sigma}(w) < \infty, \qquad \sigma = 1, 2, \tag{2.35}$$

for some $\kappa > 2$. This is the case if $A_{\sigma}(w)$ is $O(|w|^{-1-\varepsilon})$, $\varepsilon > 0$, for $|w| \to \infty$.

3. The existence of the wave operators

We prove the existence of $\tilde{\Omega}^{\rm in}_{\pm}$ and $\tilde{\Omega}^{\rm out}_{\pm}$ by means of Cook's method (Reed and Simon 1979, p 20). Thus we start from the relations

$$\tilde{\Omega}^{\rm in}(t)\psi = \tilde{\Omega}^{\rm in}(t_0)\psi + {\rm i}\int_{t_0}^{t} {\rm d}s\, U^*(s)(\tilde{H} - H^{\rm in})U^{\rm in}(s)P^{\rm in}\psi \tag{3.1}$$

and

$$\tilde{\Omega}^{\rm out}(t)\psi = \tilde{\Omega}^{\rm out}(t_0)\psi + {\rm i}\int_{t_0}^{t} {\rm d}s\, \tilde{U}^*(s)[\tilde{H} - H^{\rm out} + m_1/(q_1 s)]U^{\rm out}(s)P^{\rm out}\psi,$$
$$\psi \in \mathscr{D} \cap \mathscr{D}(q_1^{-1}). \tag{3.2}$$

The wave operators exist if the limits of the time integrals for $t\to\pm\infty$ in (3.1) and (3.2) exist for a fundamental set (i.e. a set whose linear span is dense) of $\psi\in\mathcal{H}$. This is the case if

$$\int_{t_0}^{\infty} dt\,\|(\tilde{H}-H^{\text{in}})U^{\text{in}}(t)P^{\text{in}}\psi\|<\infty, \tag{3.3}$$

respectively

$$\int_{t_0}^{\infty} dt\,\|[\tilde{H}-H^{\text{out}}+m_1/(q_1t)]U^{\text{out}}(t)P^{\text{out}}\psi\|<\infty \tag{3.4}$$

for $t\to+\infty$ in (3.1) and (3.2) with similar expressions for $t\to-\infty$. In (3.4) we take $t_0>0$ so that no problems occur with the $m_1/(q_1t)$ term in $t=0$.

We start with (3.3). It is sufficient to consider a set $\mathcal{M}$ of ψ's such that $\{P^{\text{in}}\psi\mid\psi\in\mathcal{M}\}$ is fundamental in $P^{\text{in}}\mathcal{H}$. Thus we take ($\hat{\boldsymbol{r}}_j=\boldsymbol{x}_j-\boldsymbol{X}, j=1,\ldots,N$)

$$\psi(\boldsymbol{X},\hat{\boldsymbol{r}}_1,\ldots,\hat{\boldsymbol{r}}_N)=g_1(X_1)g_2(X_2)g_3(X_3)h_k(\hat{\boldsymbol{r}}_1,\ldots,\hat{\boldsymbol{r}}_N), \tag{3.5}$$

where $g_\sigma\in\mathcal{D}(P_\sigma)\subset L^2(\mathbb{R},dX_\sigma)$, $\sigma=1, 2$, and h_k is an eigenfunction of H^{at} with associated eigenvalue ε_k. For $g_3(X_3)$ we take the functions with Fourier transforms $K\exp[-K^2/(2M)+iK\rho]$, $\rho\in\mathbb{R}$, whose linear span is dense in $L^2(\mathbb{R},dX_3)$. (The corresponding three-dimensional case is discussed by Prugovečki (1971, p 543).) Then (C_k, $k=1, 2, 3,\ldots$, denote constants in this section)

$$g_3(X_3,t)=C_1(X_3-\rho)(1+it)^{-3/2}\exp[-M(X_3-\rho)^2/2(1+it)]. \tag{3.6}$$

Now

$$\begin{aligned}\psi(t)&\equiv\exp(-iH^{\text{in}}t)\psi=\exp(-iT^{\text{CM}}t)g\otimes\exp(-i\varepsilon_kt)h_k\\&=\exp(-i\varepsilon_kt)g(t)\otimes h_k,\end{aligned} \tag{3.7}$$

where $g(t)=\exp(-iT^{\text{CM}}t)g$ and the tensor product notation is self-explanatory. Thus we obtain

$$\begin{aligned}&\|(\tilde{H}-H^{\text{in}})U^{\text{in}}(t)P^{\text{in}}\psi\|\\&\quad=\|(\tilde{H}-H^{\text{in}})g(t)\otimes h_k\|\\&\quad=\left\|\sum_{\sigma=1}^{2}\sum_{j=0}^{N}[-(e_j/m_j)A_\sigma(x_{j3})P_{j\sigma}+(e_j^2/2m_j)A_\sigma^2(x_{j3})]g(t)\otimes h_k\right\|\\&\quad\leqslant\sum_{\sigma=1}^{2}\sum_{j=0}^{N}(|e_j|/m_j)\|A_\sigma(x_{j3})P_{j\sigma}g(t)\otimes h_k\|\\&\qquad+\sum_{\sigma=1}^{2}\sum_{j=0}^{N}(e_j^2/2m_j)\|A_\sigma^2(x_{j3})g(t)\otimes h_k\|.\end{aligned} \tag{3.8}$$

We consider $\|A_1(x_{13})P_{11}g(t)\otimes h_k\|$ in some more detail. Let $\hat{\boldsymbol{q}}_j$ be the canonical momentum associated with $\hat{\boldsymbol{r}}_j$, $j=1,\ldots,N$. Then, expressing $\boldsymbol{p}_1$ in terms of $\boldsymbol{P}$ and the $\hat{\boldsymbol{q}}_j$,

$$\boldsymbol{p}_1=\lambda\boldsymbol{P}+\sum_{j=1}^{N}\mu_j\hat{\boldsymbol{q}}_j, \tag{3.9}$$

where λ and the μ_j are real constants, we obtain

$$\|A_1(x_{13})p_{11}g(t)\otimes h_k\|$$

$$\leqslant |\lambda|\,\|A_1(X_3+\hat{r}_{13})P_1g(t)\otimes h_k\|+\sum_{j=1}^{N}|\mu_j|\,\|A_1(X_3+\hat{r}_{13})g(t)\otimes \hat{q}_{j1}h_k\|$$

$$=|\lambda|\,\|\boldsymbol{P}_1g_1\|_{\mathrm{CM},1}\cdot\|g_2\|_{\mathrm{CM},2}\|A_1(X_3+\hat{r}_{13})g_3(t)\otimes h_k\|_{\mathrm{CM3,at}}$$

$$+\sum_{j=1}^{N}|\mu_j|\,\|g_1\|_{\mathrm{CM},1}\|g_2\|_{\mathrm{CM},2}\|A_1(X_3+\hat{r}_{13})g_3(t)\otimes\hat{q}_{j1}h_k\|_{\mathrm{CM3,at}} \tag{3.10}$$

where the meaning of the various norms will be clear. Let $2<\kappa<3$ and $y=(X_3-\rho)/(1+t^2)^{1/2}$. Then

$$\|A_1(X_3+\hat{r}_{13})g_3(t)\otimes h_k\|^2_{\mathrm{CM3,at}}$$

$$=C_1^2\int \mathrm{d}X_3\,\mathrm{d}\hat{\boldsymbol{r}}_1\ldots\mathrm{d}\hat{\boldsymbol{r}}_N A_1^2(X_3+\hat{r}_{13})(X_3-\rho)^2(1+t^2)^{-3/2}$$

$$\times\exp[-M(X_3-\rho)^2/(1+t^2)]|h_k(\hat{\boldsymbol{r}}_1,\ldots,\hat{\boldsymbol{r}}_N)|^2$$

$$=C_1^2\int \mathrm{d}\hat{\boldsymbol{r}}_1\ldots\mathrm{d}\hat{\boldsymbol{r}}_N\,\mathrm{d}y\,|(1+t^2)^{1/2}y|^\kappa A_1^2((1+t^2)^{1/2}y+\hat{r}_{13}+\rho)$$

$$\times|(1+t^2)^{1/2}y|^{-\kappa}y^2\exp(-My^2)|h_k(\hat{\boldsymbol{r}}_1,\ldots,\hat{\boldsymbol{r}}_N)|^2$$

$$\leqslant C_2(1+t^2)^{-\kappa/2}\int \mathrm{d}\hat{\boldsymbol{r}}_1\ldots\mathrm{d}\hat{\boldsymbol{r}}_N E_{1,\kappa}(\hat{r}_{13}+\rho)|h_k(\hat{\boldsymbol{r}}_1,\ldots,\hat{\boldsymbol{r}}_N)|^2, \tag{3.11}$$

where

$$C_2=C_1^2\int \mathrm{d}y\,y^{2-\kappa}\exp(-My^2)<\infty \tag{3.12}$$

and

$$E_{\sigma,\kappa}(v)=\sup_{w\in\mathbb{R}}|w|^\kappa A_\sigma^2(w+v)=\sup_{w\in\mathbb{R}}|w-v|^\kappa A_\sigma^2(w),\qquad \sigma=1,2. \tag{3.13}$$

Under the condition

$$\sup_{w\in\mathbb{R}}|w|^\kappa A_\sigma^2(w)<\infty, \tag{3.14}$$

$E_{\sigma,\kappa}(\hat{r}_{13}+\rho)$ defines a multiplication operator which is $\mathrm{O}(|\hat{r}_{13}|^\kappa)$ for large $\hat{r}_{13}$. Since h_k (and also $\hat{q}_{j1}h_k$), being an atomic eigenfunction, has exponential decay (Combes and Thomas 1973), it follows that $h_k\in\mathscr{D}(E_{\sigma,\kappa}(\hat{r}_{13}+\rho))$ and consequently

$$\|A_1(X_3+\hat{r}_{13})g_3(t)\otimes h_k\|=\mathrm{O}(t^{-\kappa/2})\qquad \text{for } t\to\infty. \tag{3.15}$$

The same analysis applies to the other terms in (3.10) and in fact to all terms in (3.8) that are linear in A_σ. (The terms with $j=0$ need a slightly different treatment since $\boldsymbol{x}_0=\boldsymbol{X}-M^{-1}\sum_{j=1}^N\boldsymbol{r}_j$.) The terms in (3.8) that are quadratic in A_σ are also $\mathrm{O}(t^{-\kappa/2})$ provided

$$\sup_{w\in\mathbb{R}}|w|^\kappa A_\sigma^4(w)<\infty \tag{3.16}$$

but this is implied by (3.14) since $A_\sigma(X) \in L^\infty(\mathbb{R}, \mathrm{d}X)$. It follows that (3.3) holds, provided (3.14) is satisfied for some $\kappa > 2$ (then it holds for any κ', $0 \leq \kappa' \leq \kappa$). Then $\tilde{\Omega}_+^{\text{in}}$ and hence Ω_+^{in} exists. The proof for $\tilde{\Omega}_-^{\text{in}}$ goes in the same fashion.

We note at this point that the proof by Combes and Thomas for exponential decay of atomic and ionic eigenfunctions only applies to eigenfunctions with a corresponding eigenvalue that does not coincide with a threshold for an excitation or ionisation process. If this is the case we have to amend P^{at} and P^{ion} so that such eigenfunctions are not contained in $P^{\text{at}}\mathcal{H}^{\text{at}}$ and $P^{\text{ion}}\mathcal{H}^{\text{ion}}$. In actual experimental situations such states, if they exist at all, have never been encountered.

The existence proof for $\tilde{\Omega}_\pm^{\text{out}}$ is more complicated due to the Coulomb interaction in the exit channel and the circumstance that two fragments are present in this channel. In addition the CM and internal motions are not independent due to the presence of the vector potential. Therefore we have to extend slightly Dollard's original proof for Coulomb wave operators (Dollard 1964). It is convenient to use as coordinates the centre-of-mass coordinates $\boldsymbol{X}$ and the electronic coordinates $\boldsymbol{r}_j$ relative to the centre of mass of the ion constituted by the nucleus and electrons 2 to N. The associated canonical momenta are denoted by $\boldsymbol{P}$ and $\boldsymbol{q}_1$ to $\boldsymbol{q}_N$, respectively (see the appendix). H^{out} can be written as (2.20)

$$H^{\text{out}} = T^{\text{CM}} + T^1 + H^{\text{ion}}, \tag{3.17}$$

where T^{CM} is as before, $T^1 = \boldsymbol{q}_1^2/(2m_1)$ and

$$H^{\text{ion}} = \sum_{j=2}^{N} \tfrac{1}{2}\boldsymbol{q}_j^2 - \left(\sum_{j=2}^{N} \boldsymbol{q}_j\right)^2 \Big/ (2M_i) + \sum_{2\leq j<h\leq N} |\boldsymbol{r}_j - \boldsymbol{r}_h|^{-1} - N \sum_{j=2}^{N} \left|\boldsymbol{r}_j + m_0^{-1} \sum_{h=2}^{N} \boldsymbol{r}_h\right|^{-1}, \tag{3.18}$$

where m_1 and M_i are given in the appendix.

The interaction potential between electron 1 and the ion is given by

$$V^{1,\text{ion}} = \sum_{j=2}^{N} |\boldsymbol{r}_1 - \boldsymbol{r}_j|^{-1} - N\left|\boldsymbol{r}_1 + m_0^{-1} \sum_{h=2}^{N} \boldsymbol{r}_h\right|^{-1} = W - r_1^{-1}. \tag{3.19}$$

Now

$$W = \sum_{j=2}^{N} \left(|\boldsymbol{r}_1 - \boldsymbol{r}_j|^{-1} - \left|\boldsymbol{r}_1 + m_0^{-1} \sum_{h=2}^{N} \boldsymbol{r}_h\right|^{-1} \right) + r_1^{-1} - \left|\boldsymbol{r}_1 + m_0^{-1} \sum_{h=2}^{N} \boldsymbol{r}_h\right|^{-1} \tag{3.20}$$

is square integrable with respect to $\boldsymbol{r}_1$ and

$$\begin{aligned} \|W\|_1 &\equiv \left(\int \mathrm{d}\boldsymbol{r}_1 \, |W|^2 \right)^{1/2} \\ &\leq C_3\left(\sum_{j=2}^{N} \left|\boldsymbol{r}_j + m_0^{-1} \sum_{h=2}^{N} \boldsymbol{r}_h\right|^{1/2} \right) + m_0^{-1} \left|\sum_{h=2}^{N} \boldsymbol{r}_h\right|^{1/2} \\ &\leq C_4 \sum_{j=2}^{N} |\boldsymbol{r}_j|^{1/2}. \end{aligned} \tag{3.21}$$

Let

$$H^f = \sum_{\sigma=1}^{2} \sum_{j=0}^{N} [-(e_j/m_j)A_\sigma(x_{j3})p_{j\sigma} + (e_j^2/2m_j)A_\sigma^2(x_{j3})] \tag{3.22}$$

so that

$$\|[\tilde{H} - H^{\text{out}} + m_1/(q_1 t)]U^{\text{out}}(t)P^{\text{out}}\psi\| = \|[H^f + W - r_1^{-1} + m_1/(q_1 t)]U^{\text{out}}(t)P^{\text{out}}\psi\|$$
$$\leqslant \|H^f U^{\text{out}}(t)P^{\text{out}}\psi\| + \|WU^{\text{out}}(t)P^{\text{out}}\psi\| + \|[r_1^{-1} - m_1/(q_1 t)]U^{\text{out}}(t)P^{\text{out}}\psi\|. \tag{3.23}$$

We take

$$\psi = g(\boldsymbol{X}, \boldsymbol{r}_1)h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N), \tag{3.24}$$

where h_k is an eigenstate of H^{ion} with corresponding eigenvalue ε_k. Since $A_\sigma(x_{j3})$ depends on both X_3 and one or more of the r_{j3}'s we cannot use a factorised expression $g_1(\boldsymbol{X})g_2(\boldsymbol{r}_1)$ for $g(\boldsymbol{X}, \boldsymbol{r}_1)$. Thus we extend Dollard's choice (Dollard 1964) by taking for $g(\boldsymbol{X}, \boldsymbol{r}_1)$ the set of functions with Fourier transforms $\tilde{g}(\boldsymbol{K}, \boldsymbol{k}_1) \in \mathscr{S}(\mathbb{R}^6)$ which vanish in a tube around $\boldsymbol{k}_1 = 0$ (i.e. $\tilde{g}(\boldsymbol{K}, \boldsymbol{k}_1) = 0$, $|\boldsymbol{k}_1| < \varepsilon$). It turns out in the sequel that we have to punch a few more holes in the carrier of $\tilde{g}$. Since $\tilde{g}$ can be made to vanish on a set of arbitrarily small measure the remaining set of g's is still dense in $\mathscr{H}$. Now, following Dollard's method (see also Reed and Simon 1979, p 169),

$$g(\boldsymbol{X}, \boldsymbol{r}_1, t) \equiv [\exp(-\text{i}(T^{\text{CM}} + T^1)t)U_c'(t)g](\boldsymbol{X}, \boldsymbol{r}_1)$$
$$= g_1(\boldsymbol{X}, \boldsymbol{r}_1, t) + g_2(\boldsymbol{X}, \boldsymbol{r}_1, t), \tag{3.25}$$

where

$$g_1(\boldsymbol{X}, \boldsymbol{r}_1, t) = (\text{i}t)^{-3}(Mm_1)^{3/2} \exp[\text{i}\delta(\boldsymbol{X}, \boldsymbol{r}_1, t)]\tilde{g}(M\boldsymbol{X}/t, m_1\boldsymbol{r}_1/t), \tag{3.26}$$

with

$$\delta(\boldsymbol{X}, \boldsymbol{r}_1, t) = (M\boldsymbol{X}^2 + m_1\boldsymbol{r}_1^2)/(2t) + (m_1 t/r_1)\ln(2m_1 r_1^2/t) \tag{3.27}$$

and

$$g_2(\boldsymbol{X}, \boldsymbol{r}_1, t) = (2\pi \text{i}t)^{-3}(Mm_1)^{3/2} \exp[\text{i}(M\boldsymbol{X}^2 + m_1\boldsymbol{r}_1^2)/(2t)]R(\boldsymbol{X}, \boldsymbol{r}_1, t). \tag{3.28}$$

Here $R(\boldsymbol{X}, \boldsymbol{r}_1, t)$ has the property

$$|R(\boldsymbol{X}, \boldsymbol{r}_1, t)| \leqslant C_5 t^{-1}(1 + M\boldsymbol{X}^2/t^2 + m_1\boldsymbol{r}_1^2/t^2)^{-n}(\ln t)^{\mu}, \qquad t > \text{e}, \tag{3.29}$$

for any positive integer n and some $\mu = \mu(n) > 0$. Our formulae differ from Dollard's since we are working in six dimensions instead of three. In (3.23) we require $t > \text{e}$ instead of Dollard's $t > 1$. The reason is that different μ's can occur depending on t being smaller or larger than e, the base of the natural logarithms.

We now consider the various terms in (3.23):

$$\|WU^{\text{out}}(t)P^{\text{out}}\psi\|^2 = \int \text{d}\boldsymbol{X}\, \text{d}\boldsymbol{r}_1 \ldots \text{d}\boldsymbol{r}_N\, W^2(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)|g(t, \boldsymbol{X}, \boldsymbol{r}_1)|^2|h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2$$
$$\leqslant \int \text{d}\boldsymbol{r}_1 \ldots \text{d}\boldsymbol{r}_N\, W^2(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)|h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2 \sup_{\boldsymbol{r}_1 \in \mathbb{R}^3} \int \text{d}\boldsymbol{X}\, |g(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2$$
$$\leqslant C_6\Big(\sup_{\boldsymbol{r}_1 \in \mathbb{R}^3} \int \text{d}\boldsymbol{X}\, |g_1(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2 + \sup_{\boldsymbol{r}_1 \in \mathbb{R}^3} \int \text{d}\boldsymbol{X}\, |g_2(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2\Big). \tag{3.30}$$

Here

$$C_6 = \int \text{d}\boldsymbol{r}_1 \ldots \text{d}\boldsymbol{r}_N\, W^2|h_k|^2 < \infty \tag{3.31}$$

in view of (3.21) and the exponential decay of the ionic eigenfunction h_k.

Now

$$\int \mathrm{d}\boldsymbol{X}\ |g_1(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2 = t^{-6}(Mm_1)^3 \int \mathrm{d}\boldsymbol{X}\ |\tilde{g}(M\boldsymbol{X}/t, m_1\boldsymbol{r}_1/t)|^2$$

$$= (m_1/t)^3 \int \mathrm{d}\boldsymbol{y}\ |\tilde{g}(\boldsymbol{y}, m_1\boldsymbol{r}_1/t)|^2. \tag{3.32}$$

Since $\tilde{g} \in \mathscr{S}(\mathbb{R}^6)$ we have for any positive integer n

$$|\hat{g}(\boldsymbol{y}, m_1\boldsymbol{r}_1/t)|^2 \leq C_n[1 + y^2 + (m_1 r_1/t)^2]^{-2n} \leq C_n(1+y^2)^{-2n}, \tag{3.33}$$

so that, taking $t_0 = \mathrm{e}$,

$$\int \mathrm{d}\boldsymbol{X}\ |g_1(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2 \leq C_7 t^{-3}, \qquad t > t_0. \tag{3.34}$$

Furthermore (n positive integer)

$$\int \mathrm{d}\boldsymbol{X}\ |g_2(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2$$

$$\leq (2\pi t)^{-6}(Mm_1)^3 \int \mathrm{d}\boldsymbol{X}\ |R(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2$$

$$\leq (2\pi t)^{-6}(Mm_1)^3 C_8(\ln t)^{2\mu} t^{-2} \int \mathrm{d}\boldsymbol{X}\ (1 + MX^2/t^2 + m_1 r_1^2/t^2)^{-2n}$$

$$\leq C_9 t^{-5}(\ln t)^{2\mu}, \qquad t > t_0. \tag{3.35}$$

Thus

$$\|WU^{\mathrm{out}}(t)P^{\mathrm{out}}\psi\| \leq C_{10} t^{-3/2}, \qquad t > t_0. \tag{3.36}$$

The action of $r_1^{-1} - m_1/(q_1 t)$ on $g_1(t)$ leads to a vanishing result, whereas $\|r_1^{-1} g_2(t)\|$ and $\|[m_1/(q_1 t)]g_2(t)\|$ decay as $t^{-3/2}(\ln t)^{\mu}$ for large t (Dollard 1964, p 734). Thus it remains to consider the terms containing the vector potential. We have

$$\|H^f U^{\mathrm{out}}(t)P^{\mathrm{out}}\psi\| \leq \sum_{\sigma=1}^{2} \sum_{j=0}^{N} [(|e_j|/m_j)\|A_\sigma(x_{j3})p_{j\sigma}g(t) \otimes h_k\|$$

$$+ (e_j^2/2m_j)\|A_\sigma^2(x_{j3})g(t) \otimes h_k\|]. \tag{3.37}$$

Expressing $\boldsymbol{x}_0, \ldots, \boldsymbol{p}_N$ in terms of $\boldsymbol{X}, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{P}, \boldsymbol{q}_1, \ldots, \boldsymbol{q}_N$, according to

$$\boldsymbol{x}_j = \boldsymbol{X} + a_j \boldsymbol{r}_1 + \sum_{h=2}^{N} b_{jh}\boldsymbol{r}_h, \qquad \boldsymbol{p}_j = (m_j/M)\boldsymbol{P} + c_j \boldsymbol{q}_1 + \sum_{h=2}^{N} d_{jh}\boldsymbol{q}_h, \tag{3.38}$$

we obtain

$$\|A_1(x_{j3})P_{j1}g(t) \otimes h_k\|$$

$$\leq (m_j/M)\left\|A_1\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)P_1 g(t) \otimes h_k\right\|$$

$$+ |c_j|\left\|A_1\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)q_{11} g(t) \otimes h_k\right\|$$

$$+ \sum_{h=2}^{N} |d_{jh}|\left\|A_1\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)g(t) \otimes q_{h1} h_k\right\|. \tag{3.39}$$

For $t > t_0$ ($\boldsymbol{Y} = M\boldsymbol{X}/t$, $u = m_1\boldsymbol{r}_1/t$)

$$\left\|A_1\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)P_1 g_1(t) \otimes h_k\right\|^2$$

$$= t^{-6}(Mm_1)^3 \int \mathrm{d}\boldsymbol{X}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N\, A_1^2\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)$$

$$\times (MX_1/t)^2 |\tilde{g}(M\boldsymbol{X}/t, m_1\boldsymbol{r}_1/t)|^2 |h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2$$

$$= \int \mathrm{d}y\, \mathrm{d}\boldsymbol{u}\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_N\, A_1^2\left[\left(\frac{y_3}{M} + a_j \frac{u_3}{m_1}\right)t + \sum_{h=2}^{N} b_{jh} r_{h3}\right]$$

$$\times y_1^2 |\tilde{g}(\boldsymbol{y}, \boldsymbol{u})|^2 |h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2$$

$$= \int \mathrm{d}y\, \mathrm{d}\boldsymbol{u}\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_N \left|\frac{y_3}{M} + a_j \frac{u_3}{m_1}\right|^{\kappa} A_1^2\left[\left(\frac{y_3}{M} + a_j \frac{u_3}{m_1}\right)t + \sum_{h=2}^{N} b_{jh} r_{h3}\right]$$

$$\times \left|\frac{y_3}{M} + \sigma_j \frac{u_3}{m_1}\right|^{-\kappa} y_1^2 |\tilde{g}(\boldsymbol{y}, \boldsymbol{u})|^2 |h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2$$

$$\leqslant t^{-\kappa} \int \mathrm{d}y\, \mathrm{d}\boldsymbol{u}\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_N\, y_1^2 |\tilde{g}(\boldsymbol{y}, \boldsymbol{u})|^2$$

$$\times |(y_3/M) + (a_j u_3/m_1)|^{-\kappa} E_{1,\kappa}\left(\sum_{h=2}^{N} b_{jh} r_{h3}\right) |h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2, \tag{3.40}$$

with $E_{1,\kappa}$ given by (3.13). Again we assume that (3.14) holds for some $\kappa > 2$. For the same reasons as discussed below (3.14) the multiple integral over $\boldsymbol{r}_2$ to $\boldsymbol{r}_N$ is finite so that (3.40) is finite, provided

$$\int \mathrm{d}y\, \mathrm{d}\boldsymbol{u}\, |(y_3/M) + (a_j u_3/m_1)|^{-\kappa} y_1^2 |\tilde{g}(\boldsymbol{y}, \boldsymbol{u})|^2 < \infty. \tag{3.41}$$

This will be the case if we assume that $\tilde{g}(\boldsymbol{y}, \boldsymbol{u})$ vanishes in a tube around $m_1 y_3 + Ma_j u_3 = 0$, or equivalently around $X_3 + a_j r_{13} = 0$. Note that for $j = 0, 2, 3, \ldots, N$, $X_3 + a_j r_{13} = R_3$, the third coordinate of the ionic centre-of-mass, whereas for $j = 1$, $X_3 + a_1 r_3 = x_{13}$, the third coordinate of electron 1. (See the appendix.)

$$\left\|A_1\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)P_1 g_2(t) \otimes h_k\right\|^2$$

$$= (2\pi t)^{-6} \int \mathrm{d}\boldsymbol{X}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N\, A_1^2\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)$$

$$\times |\boldsymbol{R}'(\boldsymbol{X}, \boldsymbol{r}_1, t)|^2 |h_k(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)|^2$$

$$\leqslant (2\pi t)^{-6} \int \mathrm{d}\boldsymbol{X}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N\, A_1^2\left(X_3 + a_j r_{13} + \sum_{h=2}^{N} b_{jh} r_{h3}\right)$$

$$\times (\ln t)^{2\mu} t^{-2} C_{11} (1 + M\boldsymbol{X}^2/t^2 + m_1 \boldsymbol{r}_1^2/t^2)^{-2n} |h_k|^2$$

$$= C_{11} \int \mathrm{d}y\, \mathrm{d}\boldsymbol{u}\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_N \left|\frac{y_3}{M} + a_j \frac{u_3}{m_1}\right|^{\rho} A_1^2\left[\left(\frac{y_3}{M} + \frac{a_j u_3}{m_1}\right)t + \sum_h b_{jh} r_{h3}\right]$$

$$\times \left|\frac{y_3}{M}+\frac{a_j u_3}{m_1}\right|^{-\rho}(1+y^2/M+u^2/m_1)^{-2n}|h_k|^2$$

$$\leqslant C_{12}(\ln t)^{2\mu}t^{-2-\rho}\int \mathrm{d}y\,\mathrm{d}\boldsymbol{u}\left|\frac{y_3}{M}+\frac{a_j u_3}{m_1}\right|^{-\rho}\left|1+\frac{y^2}{M}+\frac{u^2}{m_1}\right|^{-2n}$$

$$\times \int \mathrm{d}\boldsymbol{r}_2\ldots \mathrm{d}\boldsymbol{r}_N E_\rho\Big(\sum_h b_{jh}r_{h3}\Big)|h_k|^2, \qquad t>t_0, \tag{3.42}$$

where $0<\rho<1$. The integrals are finite since the singularity in the integrand for the y, $\boldsymbol{u}$ integration is integrable for such ρ.

In arriving at (3.42) we used the fact that $P_1 g_2(t)$ obeys a relation of the type (3.29). This follows from the fact that $U^{\text{out}}(t)$ commutes with P_1 and that $P_1 g \in \mathscr{S}(\mathbb{R}^6)$ along with g itself. Combining (3.40) and (3.42) we conclude that

$$\left\|A_1\Big(X_3+a_j r_{13}+\sum_{h=2}^{N} b_{jh}r_{h3}\Big)P_1 g(t)\otimes h_k\right\| = \mathrm{O}(t^{-1-\varepsilon}) \tag{3.43}$$

for $t\to\infty$ and for some $\varepsilon>0$ provided (3.14) holds for some $\kappa>2$ and $\tilde{g}(y,\boldsymbol{u})$ vanishes in a tube around $m_1 y_3+Ma_j u_3=0$. Following the same line of reasoning, we find that the remaining terms in (3.39) and the terms in (3.37) quadratic in A_σ are also $\mathrm{O}(t^{-1-\varepsilon})$ under the same conditions. Thus (3.4) holds for a fundamental set of ψ's and consequently $\tilde{\Omega}_+^{\text{out}}$ exists. A similar proof can be given for the existence of $\tilde{\Omega}_-^{\text{out}}$.

4. Special cases

In this section we discuss briefly two special cases. The first is that of an infinitely heavy nucleus (Born–Oppenheimer approximation) and the second that of a spatially homogeneous field (long-wavelength approximation).

4.1. *The Born–Oppenheimer approximation*

Instead of (1.2) the Hamiltonian is now given by

$$H(t)=\sum_{j=1}^{N}\tfrac{1}{2}[p_j+\boldsymbol{A}(x_{j3}-\alpha^{-1}t)]^2+\sum_{1\leqslant j<h\leqslant N}|\boldsymbol{x}_j-\boldsymbol{x}_h|^{-1}-N\sum_{j=1}^{N}|\boldsymbol{x}_j|^{-1}. \tag{4.1}$$

Now the method of § 2 for the existence proof of the time-evolution operator fails, since $\hat{H}(t)$ given by

$$\hat{H}(t)=Y(t)H(t)Y(t)^{-1}-\alpha^{-1}P_3$$

$$=\sum_{j=1}^{N}\tfrac{1}{2}[\boldsymbol{p}_j+\boldsymbol{A}(x_{j3})]^2+\sum_{1\leqslant j<h\leqslant N}|\boldsymbol{x}_j-\boldsymbol{x}_h|^{-1}-N\sum_{j=1}^{N}|\boldsymbol{x}_j+\alpha^{-1}t\boldsymbol{e}_3|^{-1}-\alpha^{-1}P_3 \tag{4.2}$$

is still time dependent. (Here $Y(t)=\exp(-\mathrm{i}\alpha^{-1}P_3 t)$, where now $\boldsymbol{P}=\Sigma_{j=1}^{N}\boldsymbol{p}_j$.)

We can, however, apply Kato's results (Kato 1970). In his theorem 4.1 Kato gives a set of conditions under which $\hat{H}(t)$ (Kato uses $A(t)\equiv \mathrm{i}\hat{H}(t)$) defines a time-evolution operator $\hat{U}(t,t_0)$. Referring to Kato's paper for details we note that, since $\hat{H}(t)$ is self-adjoint with time-independent domain $\mathscr{D}=\mathscr{D}(T)$ $(T=\Sigma_{j=1}^{N}\tfrac{1}{2}\boldsymbol{p}_j^2)$, most of these conditions are automatically satisfied. For the auxiliary space $\mathscr{Y}$, used by Kato, we can take $\mathscr{D}$, equipped with the graph norm. Since $\mathscr{Y}$, thus defined, is a Hilbert space and hence reflexive and uniformly convex, the results by Kato, obtained in § 5 of his paper, also apply. The only condition that remains to be verified is condition iii of Kato's theorem 4.1. In our case this amounts to showing that

$$D(t) \equiv \sum_{j=1}^{N} |\boldsymbol{x}_j + \alpha^{-1} t \boldsymbol{e}_3|^{-1} [1+T]^{-1} \tag{4.3}$$

is continuous in t with respect to the operator norm topology of $\mathscr{B}(\mathscr{H})$ (the bounded operators on $\mathscr{H}$). Now, with $T_j = \frac{1}{2}\boldsymbol{p}_j^2$,

$$\begin{aligned} \|D(t) - D(t_0)\| & \\ &= \left\| \sum_{j=1}^{N} (|\boldsymbol{x}_j + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x}_j + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1})(1+T_j)^{-1}(1+T_j)(1+T)^{-1} \right\| \\ &\leqslant \sum_{j=1}^{N} \|(|\boldsymbol{x}_j + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x}_j + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1})[1+T_j]^{-1}\|_j \|[1+T_j][1+T]^{-1}\| \\ &\leqslant \sum_{j=1}^{N} \|(|\boldsymbol{x}_j + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x}_j + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1})[1+T_j]^{-1}\|_j, \end{aligned} \tag{4.4}$$

where $\|\cdot\|_j$ is the operator norm on $\mathscr{B}(\mathscr{H}_j)$, $\mathscr{H}_j = L^2(\mathbb{R}^3, \mathrm{d}\boldsymbol{x}_j)$. Thus we have to show that

$$\lim_{t \to t_0} \|(|\boldsymbol{x}_j + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x}_j + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1})(1+T_j)^{-1}\|_j = 0. \tag{4.5}$$

Dropping the index j for brevity we note that for $f \in L^2(\mathbb{R}^3, \mathrm{d}\boldsymbol{x})$

$$g(\boldsymbol{x}) \equiv ([1+T]^{-1} f)(\boldsymbol{x}) \tag{4.6}$$

is contained in $L^\infty(\mathbb{R}^3, \mathrm{d}\boldsymbol{x})$ and $\|g\|_\infty \leqslant C\|f\|$ with C a positive constant (Reed and Simon 1975, § IX.7). Thus

$$\|(|\boldsymbol{x} + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x} + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1})[1+T]^{-1} f\| \leqslant C \| |\boldsymbol{x} + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x} + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1} \| \|f\|. \tag{4.7}$$

Now, making a few coordinate changes, we find

$$\| |\boldsymbol{x} + \alpha^{-1} t \boldsymbol{e}_3|^{-1} - |\boldsymbol{x} + \alpha^{-1} t_0 \boldsymbol{e}_3|^{-1} \| = |(t - t_0)/\alpha| \, \| |\boldsymbol{x} + \boldsymbol{e}_3|^{-1} - |\boldsymbol{x}|^{-1} \|. \tag{4.8}$$

Since (4.8) tends to zero for $t \to t_0$ it follows that $D(t)$ converges towards $D(t_0)$ in the operator norm topology. Now Kato's results are applicable so that $\hat{U}(t, t_0)$ and hence $U(t, t_0) = Y(t)\hat{U}(t, t_0)Y(t_0)^{-1}$ exists and has the properties mentioned in § 2. The existence of the wave operators $\Omega_\pm^{\text{in}}$ and $\Omega_\pm^{\text{out}}$ (with appropriate modifications of $U^{\text{in}}(t)$ and $U^{\text{out}}(t)$) can again be proven by means of Cook's method. In fact things are somewhat simpler now since there are no CM variables. It turns out, as before, that the wave operators exist, provided (2.35) holds.

4.2. *Spatially homogeneous fields*

At optical field frequencies the corresponding wavelength is at least two orders of magnitude larger than the spatial distances characteristic for the atomic interactions. This makes it plausible to neglect the spatial dependence of $\boldsymbol{A}(\boldsymbol{x}, t)$; the so-called long-wavelength approximation. Now

$$H(t)=\sum_{j=0}^{N}(2m_j)^{-1}[\boldsymbol{p}_j-e_j\boldsymbol{A}(t)]^2+\sum_{0\leq j<h\leq N}e_je_h|\boldsymbol{x}_j-\boldsymbol{x}_h|^{-1}, \tag{4.9}$$

where we write $\boldsymbol{A}(t)$ instead of $\boldsymbol{A}(-\alpha^{-1}t)$. In this case we can no longer transform the time dependence to the potentials as was done in § 4.1. A direct application of Kato's theorems now requires the norm continuity of

$$\sum_{j=0}^{N}\{-(e_j/m_j)\boldsymbol{A}(t)\cdot\boldsymbol{p}_j+[e_j^2/(2m_j)]\boldsymbol{A}^2(t)\}[1+T]^{-1}=H^f(t)[1+T]^{-1}. \tag{4.10}$$

This will not be the case for general $A_\sigma(t)\in L^\infty(\mathbb{R},\mathrm{d}t)$. We have to assume in addition that $A_\sigma(t)$ is at least piecewise continuous. There is, however, a way out of this problem. Let

$$F(t)=\int_0^t \mathrm{d}s\, H^f(s). \tag{4.11}$$

$F(t)$ is self-adjoint with domain $\mathscr{D}(F(t))\supset\mathscr{D}$. Thus $\{\exp[\mathrm{i}F(t)],\ t\in\mathbb{R}\}$ is a family of unitary operators, which is strongly continuous in t. In addition, for $\psi\in\mathscr{D}$

$$\partial_t \exp[\mathrm{i}F(t)]\psi=\mathrm{i}H^f(t)\exp[\mathrm{i}F(t)]. \tag{4.12}$$

We consider the equation

$$\partial_t\psi(t)=-\mathrm{i}H(t)\psi(t). \tag{4.13}$$

With

$$\phi(t)=\exp[\mathrm{i}F(t)]\psi(t), \tag{4.14}$$

we obtain

$$\begin{aligned}\partial_t\phi(t)&=-\mathrm{i}\{\exp[\mathrm{i}F(t)]H(t)\exp[-\mathrm{i}F(t)]-\partial_tF(t)\}\phi(t)\\&=-\mathrm{i}\check{H}(t)\phi(t),\end{aligned} \tag{4.15}$$

where

$$\check{H}(t)=\sum_{j=0}^{N}\boldsymbol{p}_j^2/(2m_j)+\sum_{0\leq j<h\leq N}e_je_h|\boldsymbol{x}_j-\boldsymbol{x}_h+\boldsymbol{c}_{jh}(t)|^{-1}. \tag{4.16}$$

Here

$$\boldsymbol{c}_{jh}(t)=(e_j/m_j-e_h/m_h)\int_0^t\mathrm{d}s\,\boldsymbol{A}(s). \tag{4.17}$$

$\check{H}(t)$ is self-adjoint with domain $\mathscr{D}=\mathscr{D}(T)$ for each $t\in\mathbb{R}$. We can now apply Kato's results since we can show that

$$\sum_{0\leq j<h\leq N}e_je_h|\boldsymbol{x}_j-\boldsymbol{x}_h-\boldsymbol{c}_{jh}(t)|^{-1}[1+T]^{-1} \tag{4.18}$$

is continuous in t. The proof is similar to that given in § 4.1. As a result $\check{H}(t)$ generates a unitary time-evolution operator $\check{U}(t,t_0)$. It follows that the formal manipulations leading from (4.13) to (4.15) can be given a meaning and that

$$U(t,t_0)=\exp[-\mathrm{i}F(t)]\check{U}(t,t_0)\exp[\mathrm{i}F(t_0)] \tag{4.19}$$

is the time-evolution operator associated with $H(t)$. The existence of the wave operators can now again be proven under condition (2.35).

5. Discussion

In the previous sections we discussed the existence of time-evolution and wave operators for a model atom in a time-dependent field with fixed propagation direction. We used a trick to convert the problem into one with a time-independent Hamiltonian. The reason that this was possible is connected with the fact that the potential commutes with the total momentum operator. Although we neglected spin effects, it will be clear that the addition of spin–spin and spin–orbit interactions to V does not destroy this commutation property. Thus, as long as these terms have appropriate relative smallness properties with respect to $T \otimes I^s$ (I^s is the identity operator in the total spin space), the method used here can probably be extended. Note, however, that the usual form of the spin–orbit interaction terms (Messiah 1965, p 552, equation XIII.95) is too singular to be treated in this way. In a subsequent paper we shall discuss the effect of the Pauli principle for the case of spin-independent interactions. This is mainly a matter of book-keeping.

We finally discuss a few matters pertaining to the asymptotic condition on the vector potential. In an actual multiphoton ionisation experiment a laser produces a pulse of radiation which is focused by means of a lens. In this focus the ionisation process takes place. It is often assumed that the field at the time it is centred around the focus can be described by a sinusoidal field, damped by a Gaussian. In the Coulomb gauge the vector potential and the magnetic component of the electromagnetic field are related by

$$\boldsymbol{A}(\boldsymbol{x}) = \partial_{\boldsymbol{x}} \times \int \mathrm{d}\boldsymbol{x}' \, [4\pi|\boldsymbol{x}-\boldsymbol{x}'|]\boldsymbol{B}(\boldsymbol{x}') = \int \mathrm{d}\boldsymbol{x}' \, (4\pi|\boldsymbol{x}-\boldsymbol{x}'|^2)^{-1} \boldsymbol{e}_{\boldsymbol{x}-\boldsymbol{x}'} \times \boldsymbol{B}(\boldsymbol{x}'). \tag{5.1}$$

This relation holds for $\boldsymbol{B} \in \mathscr{S}$ (i.e. $B_\alpha \in \mathscr{S}$, $\alpha = 1, 2, 3$) in which case also $\boldsymbol{A} \in \mathscr{S}$. It is then easily generalised to more general $\boldsymbol{B}$ fields, using the estimate

$$|\boldsymbol{A}(\boldsymbol{x})| \leqslant \int \mathrm{d}\boldsymbol{x}' \, (4\pi|\boldsymbol{x}-\boldsymbol{x}'|^2)^{-1} |\boldsymbol{B}(\boldsymbol{x}')| \tag{5.2}$$

and the Sobolev inequality. In particular it follows that for square integrable $\boldsymbol{B}$ (as is the case for an electromagnetic field with finite energy), $\boldsymbol{A}(\boldsymbol{x}) \in L^6(\mathbb{R}^3, \mathrm{d}\boldsymbol{x})$. This does not necessarily imply that $\boldsymbol{A}(\boldsymbol{x})$ vanishes for large $\boldsymbol{x}$ but if $\boldsymbol{B}(\boldsymbol{x})$ is a smooth function obeying

$$\boldsymbol{B}(\boldsymbol{x}) \leqslant c(a^2 + r^2)^{-\alpha}, \qquad c, a^2 > 0, \tag{5.3}$$

then it follows from (5.2), by first performing the integration over the angles in $\boldsymbol{x}'$, that

$$\begin{aligned} |\boldsymbol{A}(\boldsymbol{x})| &= \mathrm{O}(r^{-2\alpha+1}), \qquad && \tfrac{1}{2} < \alpha < \tfrac{3}{2}, \\ |A(\boldsymbol{x})| &= \mathrm{O}(r^{-2+2\varepsilon}), \qquad && \alpha \geqslant \tfrac{3}{2}, \ \varepsilon > 0. \end{aligned} \tag{5.4}$$

(Note that for $\alpha > \frac{3}{4}$ in (5.3), $\boldsymbol{B}(\boldsymbol{x})$ is square integrable.) Thus we see that for $\boldsymbol{B}(\boldsymbol{x})$ decaying sufficiently fast, $A(\boldsymbol{x})$ is also decaying. Equation (5.2) applies to $\boldsymbol{B}$ and $\boldsymbol{A}$, evaluated at some specific time t_0. This raises the question whether there is decay for other times t. This is indeed the case. If $\boldsymbol{B}(\boldsymbol{x}, t_0) \in \mathscr{S}$ then also $\boldsymbol{B}(\boldsymbol{x}, t) \in \mathscr{S}$, so that $\boldsymbol{A}(\boldsymbol{x}, t) \in \mathscr{S}$. The situation for $\boldsymbol{B}(\boldsymbol{x}, t_0)$ obeying (5.3) is more complicated, but results similar to (5.4) can be obtained. In the model discussed in this paper we therefore assumed that $A(u) = \mathrm{O}(|u|^{-1-\varepsilon})$. At the expense of significant technical complications it is possible to relax this condition. This does not seem worthwhile in view of the experimental situation. It is far more realistic to assume that the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields are sinusoidal fields, damped by a Gaussian. Thus, in the linearly polarised case, let $E_1(u) = cB_2(u) = E_0 \sin(\omega u) \exp(-\alpha u^2)$, $E_2 = B_1 = 0$. Then these fields are derivable from $\boldsymbol{A}(u)$ with $A_2(u) = 0$ and

$$A_1(u) = -(E_0/c) \int_u^\infty \mathrm{d}u' \sin(\omega u') \exp[-\alpha (u')^2] \tag{5.5}$$

which quantity decays as a Gaussian for large $|u|$.

In principle we can spoil the asymptotic behaviour of $\boldsymbol{A}(u)$ by making a gauge transformation. Thus let

$$\begin{aligned} &\boldsymbol{A}(\boldsymbol{x}, t) \to \boldsymbol{A}'(\boldsymbol{x}, t) = \boldsymbol{A}(\boldsymbol{x}, t) + \partial_{\boldsymbol{x}} \chi(\boldsymbol{x}, t), \\ &0 = \Phi(\boldsymbol{x}, t) \to \Phi'(\boldsymbol{x}_0 t) = -\partial_t \chi(\boldsymbol{x}, t). \end{aligned} \tag{5.6}$$

Now $H(t) = H(\boldsymbol{A}(t))$ (equation (1.2)) with $\boldsymbol{A}(t)$ in the Coulomb gauge changes into

$$H'(t) = H(\boldsymbol{A}'(t)) - \sum_{j=0}^{N} e_j \Phi'(\boldsymbol{x}_j, t), \tag{5.7}$$

with the corresponding time-evolution operator $U(t, t_0)'$. With

$$G(t) = G(\boldsymbol{x}_0, \ldots, \boldsymbol{x}_N, t) = \exp\left(\mathrm{i} \sum_{j=0}^{N} e_j \chi(\boldsymbol{x}, t)\right), \tag{5.8}$$

we find for sufficiently smooth $\chi(\boldsymbol{x}, t)$ that

$$U(t, t_0)' = G(t) U(t, t_0) G^{-1}(t_0). \tag{5.9}$$

Defining the new channel wave-operators in the same way, i.e.

$$U^\alpha(t, t_0)' = G(t) U^\alpha(t, t_0) G^{-1}(t_0), \qquad \alpha \in \{\text{in}, \text{out}\}, \tag{5.10}$$

we obtain

$$(\Omega_\pm^\alpha(t_0))' = \operatorname*{s-lim}_{t \to \pm\infty} U(t, t_0)' U^\alpha(t, t_0)' = G(t_0) \Omega_\pm^\alpha G^{-1}(t_0) \tag{5.11}$$

so that the gauge-transformed scattering operator is

$$\begin{aligned} S'(t_0) &= (\Omega_+^{\text{out}}(t_0)')^* \Omega_-^{\text{in}}(t_0)' = G(t_0) \Omega_+^{\text{out}}(t_0) \Omega_-^{\text{in}}(t_0) G^{-1}(t_0) \\ &= G(t_0) S G^{-1}(t_0). \end{aligned} \tag{5.12}$$

Here we have to keep in mind that, although $G(t)$ is a unitary operator for $\chi(\boldsymbol{x}, t) \in L^\infty(\mathbb{R}^3, \mathrm{d}\boldsymbol{x})$, $\forall t \in \mathbb{R}$, derivatives of χ occurring in $\boldsymbol{A}'$ and Φ' may lead to self-adjointness problems for the Hamiltonians. In making a gauge transformation we should also change the states $(f \to G(t_0) f)$ so that S-matrix elements (Sf, g) are invariant. This is understandable from the fact that (5.9) defines a unitary transformation of the operators, resulting in (5.12), even in the absence of any field. The situation in the classical case is similar; the equations of motion for $\boldsymbol{x}(t)$ and $\boldsymbol{v}(t)$ are not affected by gauge transformation, since they contain $\boldsymbol{B}$ and $\boldsymbol{E}$, rather than $\boldsymbol{A}$. In the Hamiltonian formalism the time development of the system is fixed, once the initial coordinates $\boldsymbol{x}(t_0)$ and momenta $\boldsymbol{p}(t_0)$ and the Hamiltonian are given. Under a gauge transformation both the Hamiltonian and the initial momentum ($\boldsymbol{p}(t_0) \to \boldsymbol{p}'(t_0) = \boldsymbol{p}(t_0) - c\,\partial_x \chi(t_0)$) are transformed. If we do not transform $\boldsymbol{p}(t_0)$ wrong results for $\boldsymbol{x}(t)$ and $\boldsymbol{v}(t)$ can occur.

In the light of this it is somewhat surprising that there exists a subclass of gauge functions $\chi(\boldsymbol{x}, t)$ such that measurable quantities are not affected by the corresponding gauge-transformations, even if the states are not transformed (Aharonov and Au 1979, Haller and Sohn 1979). These gauge functions have the property that $\chi(\boldsymbol{x}, t_0)$ vanishes for large $|\boldsymbol{x}|$ (t_0 is fixed). That this can happen in scattering processes is understandable from the classical case, discussed above. In a scattering process the particle is initially far away from the scattering centre. But for large $\boldsymbol{x}$ the gauge function vanishes so that the gauge-transformed initial momentum coincides with the original one.

In a sequel to the present work, where we are going to relate the wave operators, discussed here, to measurable quantities, we intend to give a new proof of this gauge invariance, starting from the transformations (5.12). There we shall also show that observable quantities do not depend on the parameter t_0.

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Appendix

In this appendix we give the relation between the coordinates $\boldsymbol{x}_0, \ldots, \boldsymbol{x}_N$ and associated momenta $\boldsymbol{p}_0, \ldots, \boldsymbol{p}_N$ and the coordinates $\boldsymbol{X}, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ and associated momenta $\boldsymbol{P}$, $\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N$. The nucleus has mass M, the electrons mass m ($m = 1$ in atomic units). The mass of the ion consisting of the electrons $2, \ldots, N$ and the nucleus is $M_i = M + (N-1)m$. We denote the coordinate vector of the ionic centre of mass by $\boldsymbol{R}$, see also figure 1. We have

$$M\boldsymbol{X} = m_0\boldsymbol{x}_0 + m\sum_{j=1}^{N} \boldsymbol{x}_j, \qquad M_i\boldsymbol{R} = m_0\boldsymbol{x}_0 + m\sum_{j=2}^{N} \boldsymbol{x}_j, \tag{A1}$$

and $\boldsymbol{r}_j$ is defined by

$$\boldsymbol{r}_j = \boldsymbol{x}_j - \boldsymbol{R}, \qquad j = 0, \ldots, N. \tag{A2}$$

Then

$$\begin{aligned} \boldsymbol{x}_0 &= \boldsymbol{X} - (m/M)\boldsymbol{r}_1 - (m/m_0)\sum_{j=2}^{N} \boldsymbol{r}_j, \\ \boldsymbol{x}_1 &= \boldsymbol{X} + [1 - (m/M)]\boldsymbol{r}_1 = \boldsymbol{X} + (M_i/M)\boldsymbol{r}_1, \\ \boldsymbol{x}_j &= \boldsymbol{X} + \boldsymbol{r}_j - (m/M)\boldsymbol{r}_1, \qquad j = 2, \ldots, N. \end{aligned} \tag{A3}$$

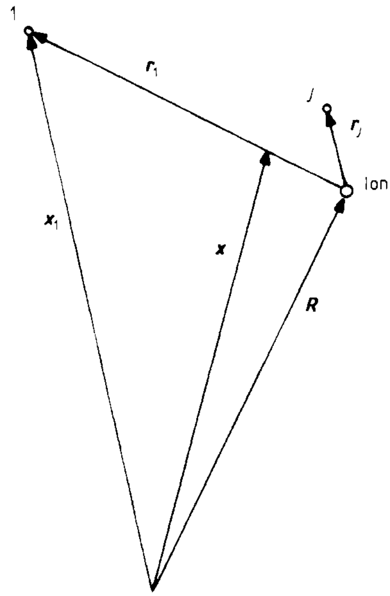

Figure 1. Picture of the various coordinates employed in the existence proof for the outgoing wave-operator in § 3.

For the momenta we have

$$p_0=(m_0/M)P-(m_0/M_i)q_1-[m_0/(m_0+m)]\sum_{j=2}^{N}q_j,$$

$$p_1=(m/M)P+q_1, \qquad \text{(A4)}$$

$$p_j=(m/M)P-(m/M_i)q_1+[m_0/(m_0+m)]q_j, \qquad j=2,\ldots,N.$$

In terms of the new momenta the kinetic energy is given by

$$T\equiv\sum_{j=0}^{N}p_j^2/(2m_j)=P^2/(2M)+q_1^2/(2m_1)+\sum_{j=2}^{N}q_j^2/(2m_j)-\left(\sum_{j=2}^{N}q_j\right)^2\Big/(2M_i), \qquad \text{(A5)}$$

where $m_1=mM_i/M$.

References

Agostini P, Clement M, Fabre F and Petite M 1981 *J. Phys. B: At. Mol. Phys.* **14** L491–5
Aharonov A and Au C K 1979 *Phys. Rev.* A **20** 1553–62
Boreham B W and Hughes J L 1981 *Sov. Phys.-JETP* **53** 252–9
Combe P, Mourre E and Richard J-L 1975 *Commun. Math. Phys.* **43** 161–70
Combes J M and Thomas L 1973 *Commun. Math. Phys.* **34** 251–70
Dollard J D 1964 *J. Math. Phys.* **5** 729–38
Haller K and Sohn R B 1979 *Phys. Rev.* A **20** 1541–52
Jörgens K and Weidmann J 1970 *Spectral Properties of Hamiltonian Operators, Lecture Notes in Mathematics* 313 (Berlin: Springer)
Kato T 1953 *J. Math. Soc. Japan* **5** 208–33
—— 1966 *Perturbation theory for linear operators* (Berlin: Springer)
—— 1970 *J. Fac. Sci. Univ. Tokyo Sect I A Math.* **17** 241–58

Messiah A 1965 *Quantum Mechanics* II (Amsterdam: North-Holland)
Prugovečki E 1971 *Quantum Mechanics in Hilbert Space* (New York: Academic)
Reed M and Simon B 1975 *Methods of Modern Mathematical Physics* II *Fourier Analysis, Self-Adjointness* (New York: Academic)
—— 1979 *Methods of Modern Mathematical Physics* III *Scattering Theory* (New York: Academic)
Schechter 1971 *Spectra of partial differential operators* (Amsterdam: North-Holland)
Yosida K 1968 *Functional Analysis* (Berlin: Springer)