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The basis generator method: optimized dynamical representation of the solution of time-dependent quantum problems

O J Kroneisen, H J Lüdde, T Kirchner and R M Dreizler
Institut für Theoretische Physik der Universität, 60054 Frankfurt, Germany

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Abstract. The theoretical investigation of time-dependent quantum systems requires the solution of the time-dependent Schrödinger (Dirac) equation. The basis generator method presented here allows a systematic construction of dynamically adapted wavefunctions based on a decomposition of the Hilbert space into a hierarchical structure of finite subspaces. For the class of interactions obeying an inverse integer power law, e.g., Coulomb and polarization interactions, an explicit representation of the dynamically optimized basis set is given.

1. Introduction

The investigation of explicitly time-dependent quantum systems covers a great variety of different topics, e.g. atoms and molecules in high intensity femtosecond laser pulses [1] or the scattering of highly charged ions by atoms, ions, molecules, clusters or solids [2, 3] in a wide range of collision energies. The large number of time-dependent systems which are of current interest corresponds with different, often quite specialized theoretical approaches for the solution of the respective time-dependent Schrödinger (Dirac) equation (TDSE) [4]. This includes the method of *finite differences* [5, 6] and *basis set expansion* methods, either built upon atomic (single-centre [7], two-centre [8–10], three-centre AO [11], and Sturmian expansions [12]) or molecular orbitals (MO expansions [13], and complex MO theory [14,15]), usually including additional pseudostates.

Focusing on collisional physics as an example of a time-dependent quantum system, the main features of these different approaches are the following: Basis set expansion methods yield reasonably accurate results for excitation and charge transfer cross sections in a very economical way. This is due to the fact that the relevant excitation and capture states are, in general, contained within the basis set. However, standard basis sets are built from a geometric, i.e. *static*, point of view. As far as ionization is concerned, usually no detailed results can be obtained from standard basis sets. If the basis set is built upon states that form a *complete* set, exact results for ionization can be obtained in the limit of an infinite number of basis states. However, this limit cannot be reached in practice.

Finite-difference methods on the other hand have the very appealing feature of accounting for excitation, charge transfer and ionization with nearly the same accuracy. The precise exploitation of finite-difference models implies the use of grids with a very large number of points. If this criterion is not met, the results for excitation, charge transfer and ionization turn

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out to be unsatisfactory. The reason for the need for large grids is that it is not possible to introduce any of the relevant aspects of physics into the construction of the grid.

The question thus arises, how to find a *systematic* and *economical* approach to the description of time-dependent quantum systems that is *not restricted* to a subset of the important physical processes. As the approach should be economical, it is obvious that it cannot be based on 'complete' basis sets or 'large' grids (which simply is another characterization of completeness). It is also obvious that it is therefore important to introduce as much as possible of the underlying specific physical structure into the construction of the method. This implies that a *dynamical* point of view should be inherent in the approach. The problem outlined here arises in different time-dependent quantum systems, so we begin with some general arguments on dynamical quantum systems.

A system whose time evolution is determined by the TDSE is characterized by just *one* wavefunction, i.e. the solution of the TDSE for the appropriate initial condition. This fact implies that the part of Hilbert space that is addressed by the solution of the TDSE at any time is only *one-dimensional*. As a consequence, it is not necessary to use large basis sets to describe the time evolution of the quantum system: *completeness* of a basis set is irrelevant for the precision of the results obtained—if only a basis has been chosen that covers that part of the Hilbert space that is relevant during the time evolution of the system. It is clear that such a basis has to be explicitly time-dependent in general, and will strongly depend on the characteristics of the quantum system *and* its initial condition. It is, however, possible to outline a theoretical description of how to create a suitable time-dependent basis set for *arbitrary* time-dependent quantum systems.

In this paper, we will therefore start the discussion with a general analysis of time-dependent quantum systems. In order to build a suitable basis, the Schrödinger operator of the time-dependent system itself is used to define the functions in the basis set. This leads to a basis set expansion that is dynamically adapted to the time evolution of the quantum system under investigation. Then we concentrate on the case of collisional systems. It will be shown that it is possible to derive *explicit* expressions for an appropriate time-dependent basis set if one, for example, focuses on pure Coulomb systems.

In a previous publication [16], we have already shown how a basis can be constructed by repeated application of the Schrödinger operator on a set of generating functions leading to a *hierarchy of states*. In order to determine the explicit form of the corresponding wavefunctions, an approximation to the exact hierarchy of states has been suggested. Despite the—at first glance—rather crude approximation of [16], practical calculations based on this formalism have shown to be accurate [17–21] for Coulomb systems. Here, we show how the previous results can be understood and improved using a different approach to the generation of the same hierarchy of states. This leads to a concept which we refer to as the *basis generator method* (BGM). Although we study the validity of the BGM concept exclusively for the case of Coulomb systems and a class of similar interactions, we emphasize that the concept also applies for other types of time-dependent quantum systems.

We start the discussion of the BGM concept with an outline of the general theory of the TDSE in a basis-set expansion and define the hierarchy of states by repeated application of the Schrödinger operator (section 2). In section 3, we show under which conditions a representation space can be found that exactly contains the hierarchy of states of section 2. We then investigate the special case of the Coulomb interaction in section 4 and derive an explicit expression of the corresponding *BGM basis*. It will be explained how the TDSE can be solved using these results in terms of a coupled channel calculation. Finally, we demonstrate in section 5 that the results of section 4 can be generalized to the entire class of potentials that can be expressed as a series in inverse integer powers of the radial distance.

2. General theory—the BGM concept

The time-dependent quantum system under consideration is specified by a Hamiltonian $\hat{H}(t)$ which can be divided into a stationary part $\hat{H}_0$ and a time-dependent potential $\hat{V}(t)$ that vanishes for asymptotic times. Given the initial condition $|\Psi_0\rangle \equiv |\Psi(t_0)\rangle$, the time evolution of a non-relativistic quantum system is completely determined by the TDSE, specified below in the interaction picture defined by $\hat{H}_0$ (with $t_0 \to -\infty$):

$$\begin{aligned}
&\hat{O}_{\mathrm{I}}(t)|\Psi_{\mathrm{I}}(t)\rangle = (\hat{H}_{\mathrm{I}}(t) - \mathrm{i}\partial_t)|\Psi_{\mathrm{I}}(t)\rangle = (\hat{V}_{\mathrm{I}}(t) - \mathrm{i}\partial_t)|\Psi_{\mathrm{I}}(t)\rangle = 0 \\
&|\Psi_{\mathrm{I}}(t)\rangle = \exp[\mathrm{i}\hat{H}_0(t-t_0)]|\Psi(t)\rangle \\
&\hat{V}_{\mathrm{I}}(t) = \exp[\mathrm{i}\hat{H}_0(t-t_0)]\hat{V}(t)\exp[-\mathrm{i}\hat{H}_0(t-t_0)] \\
&\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \qquad \lim_{t\to\pm\infty}\hat{H}(t) = \hat{H}_0.
\end{aligned} \tag{2.1}$$

The index I indicates that operators and states are given in the interaction picture. Operators and states in the Schrödinger picture are not explicitly characterized by a specific index.

For any given initial state $|\Psi_0\rangle$, the solution of the TDSE defines a one-dimensional, time-dependent subspace of the Hilbert space. The aim is therefore to find a finite basis set of time-dependent states $\{|\phi_v^u(t)\rangle\}$ such that the corresponding *finite, but time-dependent* subspace (denoted as $\mathcal{A}$) of the Hilbert space contains the solution $|\Psi_{\mathrm{I}}(t)\rangle$ for any time.

For the moment, let us consider an *arbitrary* model space $\mathcal{A}$. We define the projector on $\mathcal{A}$ as $\hat{A}$, and its complement as $\hat{B} = 1 - \hat{A}$. Following the arguments given in [16], we obtain the TDSE in $\mathcal{A}$

$$\begin{aligned}
&\hat{A}\hat{O}_{\mathrm{I}}(t)\hat{A}|\Psi_{\mathrm{I}}^{\mathrm{A}}(t)\rangle = \hat{V}_{\mathrm{I}}^{\mathrm{opt}}(t)|\Psi_{\mathrm{I}}^{\mathrm{A}}(t)\rangle \\
&\hat{V}_{\mathrm{I}}^{\mathrm{opt}}(t)|\Psi_{\mathrm{I}}^{\mathrm{A}}(t)\rangle = \mathrm{i}\hat{A}\hat{O}_{\mathrm{I}}(t)\int_{t_0}^{t}\hat{B}_{\mathrm{I}}(t,t')\hat{O}_{\mathrm{I}}(t')|\Psi_{\mathrm{I}}^{\mathrm{A}}(t')\rangle\,\mathrm{d}t'
\end{aligned} \tag{2.2}$$

with $\hat{B}_{\mathrm{I}}(t,t')$ denoting the propagator in $\mathcal{B}$-space and $V_{\mathrm{I}}^{\mathrm{opt}}(t)$ the optical potential which globally allows for an exchange of density between the spaces $\mathcal{A}$ and $\mathcal{B}$. If $\mathcal{A}$ is spanned by a finite orthonormal set of basis states $\{|\Omega_j(t)\rangle,\ j = 1,\ldots,J\}$, the corresponding so-called *coupled channel equations* can be written as

$$\begin{aligned}
\mathrm{i}\dot{c}_k(t) = &\sum_{j=1}^{J} c_j(t)\langle\Omega_k(t)|\hat{O}_{\mathrm{I}}(t)|\Omega_j(t)\rangle \\
&-\mathrm{i}\sum_{j=1}^{J}\int_{t_0}^{t} c_j(t')\langle\Omega_k(t)|\hat{O}_{\mathrm{I}}(t)\hat{B}_{\mathrm{I}}(t,t')\hat{O}_{\mathrm{I}}(t')|\Omega_j(t')\rangle\,\mathrm{d}t'
\end{aligned} \tag{2.3}$$

with the coefficients $c_k(t) = \langle\Omega_k(t)|\Psi_{\mathrm{I}}^{\mathrm{A}}(t)\rangle$ representing the $\mathcal{A}$-space part of the *exact* solution of the TDSE. For an arbitrary choice of $\mathcal{A}$, in general *each* $\mathcal{A}$-space channel $|\Omega_j(t)\rangle$ is coupled to the complementary space $\mathcal{B}$ via the optical potential $V_{\mathrm{I}}^{\mathrm{opt}}(t)$.

We choose a finite set of eigenstates of $\hat{H}_0$ which we shall call the *generating basis* as a starting point for the construction of a dynamically adapted model space $\mathcal{A}$

$$\hat{H}_0|\phi_v^0(t)\rangle = \epsilon_v|\phi_v^0(t)\rangle \qquad v = 1,\ldots,V. \tag{2.4}$$

According to [16], the full model space $\mathcal{A} \equiv \mathcal{A}^{UV}$ is then spanned in terms of a *hierarchy of states* defined by the Schrödinger operator $\hat{O}_{\mathrm{I}}(t) = (\hat{V}_{\mathrm{I}}(t) - \mathrm{i}\partial t)$ as

$$\begin{aligned}
|\phi_v^u(t)\rangle &= (\hat{V}_{\mathrm{I}}(t) - \mathrm{i}\partial_t - \epsilon_v)|\phi_v^{u-1}(t)\rangle \\
&= (\hat{V}_{\mathrm{I}}(t) - \mathrm{i}\partial_t - \epsilon_v)^u|\phi_v^0(t)\rangle \qquad u = 1,\ldots,U, \quad v = 1,\ldots,V.
\end{aligned} \tag{2.5}$$

The additional term ϵ_v has been introduced to remove trivial dependences between states of different hierarchical order. We emphasize—with respect to the discussion in section 3—that

these additional terms obviously leave the space $\mathcal{A}^{UV}$ invariant. The states $\{|\phi_v^u\rangle\}$ are linearly independent (but in general not orthonormal) except for the trivial case that the hierarchy (2.5) is closed under the operation $(\hat{V}_{\rm I}(t) - {\rm i}\partial t)$. Moreover, we have shown in [16] that only states of highest order $u = U$ can be coupled to $\mathcal{B}$-space via the optical potential $V_{\rm I}^{\rm opt}(t)$. Thus, the coupled channel equations in $\mathcal{A}^{UV}$ reduce to

$$\begin{aligned}
{\rm i}\sum_{u=0}^{U}\sum_{v=1}^{V}\dot{c}_v^u(t)\langle\phi_k^j(t)|\phi_v^u(t)\rangle &= \sum_{u=0}^{U}\sum_{v=1}^{V}c_v^u(t)\langle\phi_k^j(t)|\hat{O}_{\rm I}(t)|\phi_v^u(t)\rangle \qquad j < U \\
{\rm i}\sum_{u=0}^{U}\sum_{v=1}^{V}\dot{c}_v^u(t)\langle\phi_k^j(t)|\phi_v^u(t)\rangle &= \sum_{u=0}^{U}\sum_{v=1}^{V}c_v^u(t)\langle\phi_k^j(t)|\hat{O}_{\rm I}(t)|\phi_v^u(t)\rangle \\
&\quad -{\rm i}\sum_{v=1}^{V}\int_{t_0}^{t}c_v^U(t')\langle\phi_k^{U+1}(t)|\hat{B}_{\rm I}^{UV}(t,t')|\phi_v^{U+1}(t')\rangle\,{\rm d}t' \qquad j = U.
\end{aligned} \tag{2.6}$$

On the other hand, the population of the states $\{|\phi_v^u(t)\rangle\}$ decreases with increasing order u due to the fact that an increasing number of successive interactions is required to reach a higher subspace of the hierarchy. In this way, the action of the optical potential on the states of the finite model space $\mathcal{A}^{UV}$ is minimized—independent of the particular choice of the time-dependent interaction $\hat{V}(t)$. In this sense, the finite model space $\mathcal{A}^{UV}$ can be regarded as a *dynamically optimized representation* of the solution of the TDSE.

The role of the order U of the hierarchy of states as a parameter of convergence of the model space $\mathcal{A}^{UV}$ is based on the fact that the TDSE in its time-discretized version can be described by a finite sequence of actions of the Schrödinger operator on the physical initial condition. As long as the order U of the hierarchy of states is larger than the number of time-steps needed to discretize the TDSE, the reduced coupling scheme of (2.6) ensures that the time evolution of the quantum system is contained within the model space $\mathcal{A}^{UV}$. Although there is no possibility to determine the velocity of convergence *a priori*, practical experience shows that orders $U = 6$–12 of the hierarchy of states are usually sufficient to achieve convergence [17–21].

We emphasize that the aim of this strategy is to select a basis that is able to represent the *relevant* part of the Hilbert space for the time-dependent quantum system under investigation. This implies that the model space $\mathcal{A}^{UV}$ highly depends on the structure of the interaction potential $\hat{V}(t)$ from which it is generated.

The hierarchy of states $\{|\phi_v^u(t)\rangle\}$ can be obtained by means of the recursion relation (2.5), both in the interaction picture (noted as $\{|\phi_v^u(t)\rangle\}$) or the Schrödinger picture (noted as $\{|\varphi_v^u(t)\rangle\}$, with $\partial_t|\varphi_v^0\rangle = 0$):

$$\begin{aligned}
|\phi_v^u(t)\rangle &= (\hat{V}_{\rm I}(t) - {\rm i}\partial_t - \epsilon_v)|\phi_v^{u-1}(t)\rangle \\
&= \exp[{\rm i}\hat{H}_0(t-t_0)](\hat{H}_0 - \epsilon_v + \hat{V}(t) - {\rm i}\partial_t)|\varphi_v^{u-1}(t)\rangle \\
\Rightarrow |\varphi_v^u(t)\rangle &= (\hat{H}_0 - \epsilon_v + \hat{V}(t) - {\rm i}\partial_t)|\varphi_v^{u-1}(t)\rangle.
\end{aligned} \tag{2.7}$$

Using this relation and equation (2.4), the states of the orders $u = 1, \ldots, 3$ can explicitly be written in the Schrödinger picture (which we use exclusively from here on) as

$$\begin{aligned}
|\varphi_v^1(t)\rangle &= \hat{V}(t)|\varphi_v^0\rangle \\
|\varphi_v^2(t)\rangle &= (-\tfrac{1}{2}\Delta\hat{V}(t) + \hat{V}(t)^2 - {\rm i}\partial_t\hat{V}(t) - \nabla\hat{V}(t)\cdot\nabla)|\varphi_v^0\rangle \\
|\varphi_v^3(t)\rangle &= (\tfrac{1}{4}\nabla^4\hat{V}(t) - (\nabla\hat{V}(t))^2 - \tfrac{3}{2}\hat{V}(t)\Delta\hat{V}(t) + {\rm i}\partial_t\Delta\hat{V}(t) + \hat{V}(t)^3 \\
&\quad -3\hat{V}(t){\rm i}\partial_t\hat{V}(t) - \partial_t^2\hat{V}(t) + \nabla^3\hat{V}(t)\cdot\nabla - 3\hat{V}(t)\nabla\hat{V}(t)\cdot\nabla \\
&\quad +2{\rm i}\partial_t\nabla\hat{V}(t)\cdot\nabla + \nabla(\nabla\hat{V}(t)\cdot\nabla)\cdot\nabla + \nabla\hat{V}(t)\cdot\nabla\hat{V}_0)|\varphi_v^0\rangle
\end{aligned} \tag{2.8}$$

for an effective one-particle system with $\hat{H}_0 = -\frac{1}{2}\Delta + \hat{V}_0$. The properties of the states $\{|\varphi_v^u(t)\rangle\}$ are therefore determined by the generating basis $\{|\varphi_v^0\rangle\}$ and its derivatives, the potential $\hat{V}_0$ of

the undisturbed system and its derivatives with respect to spatial coordinates, and the structure of the time-dependent interaction $\hat{V}(t)$. The basis set $\{|\varphi_v^u(t)\rangle\}$ is adapted to the time evolution of $|\Psi(t)\rangle$ via the potential $\hat{V}(t)$. In equation (2.8), derivatives of $\hat{V}(t)$ occur. This leads to terms which are proportional to the external control variables of the time-dependent system (e.g., the velocity in a collisional process, the frequency in a laser field etc). The states $|\varphi_v^u(t)\rangle$, $u > 1$, are thus dependent on these variables. As can be seen from equation (2.8), the potential $\hat{V}_0$ of the undisturbed quantum system influences the hierarchy of states in two different ways: $\hat{V}_0$ determines the eigenstates of the undisturbed quantum system which we use as the generating basis $\{|\varphi_v^0\rangle\}$, and $\hat{V}_0$ modifies the behaviour of the time-dependent states $|\varphi_v^u(t)\rangle$, $u > 2$. We mention that the asymmetry of equation (2.8) with respect to $\hat{V}(t)$ and $\hat{V}_0$ is a result of the use of the eigenvalue equation (2.4).

The approximation used in our previous publication [16] was based on neglecting all but the pure potential terms $\hat{V}(t)^u$ in the equation for $|\varphi_v^u(t)\rangle$. In general, this approximation is expected to be too crude. In the following section we apply the hierarchy of states in a different fashion, which allows us to take into account *all* terms of equation (2.8). For the special case of $\hat{V}(t)$ being a Coulomb potential (see section 4), we demonstrate that the approximation used in [16] turns out to be better justified than can be expected at first glance.

3. The BGM strategy

As may be seen from equation (2.8), the structure of the states $\{|\varphi_v^u(t)\rangle\}$ becomes very involved with increasing order u. For given $\hat{V}(t)$, it is therefore useful to introduce an alternative set of states $\{|\chi_\nu^\mu(t)\rangle, \nu = 1, \ldots, N, \mu = 0, \ldots, M\}$ generating the same or even a larger model space. The basic idea of this *BGM strategy* is to determine functions with a simpler structure

$$|\chi_\nu^\mu(t)\rangle = X(\hat{V}(t))^\mu |\chi_\nu^0\rangle. \tag{3.1}$$

$\{|\chi_\nu^0\rangle\}$ defines a new generating basis, already containing all kinds of 'static properties' (i.e. terms of the type $\hat{V}_0, \nabla\hat{V}_0, \ldots |\varphi_v^0\rangle$) and derivative terms (i.e. $\nabla^n|\varphi_v^0\rangle$), while $X(\hat{V}(t))$ accounts for the dynamical adaptation of the basis to the time-dependent interaction potential $\hat{V}(t)$. These states span a new time-dependent model space $\mathcal{R}^{MN}$ with

$$\mathcal{A}^{UV} \subseteq \mathcal{R}^{MN} \equiv [|\chi_\nu^\mu(t)\rangle, \nu = 1, \ldots, N, \mu = 0, \ldots, M]. \tag{3.2}$$

For any given (U, V), the numbers $M(U, V)$ and $N(U, V)$ have to be determined. We show that the following two conditions are sufficient for the validity of equation (3.2). First, the generating basis of the hierarchy of states (including the physical initial condition) must be contained in $\mathcal{R}^{0N}$

$$|\Psi_0\rangle = |\Psi(t_0)\rangle \in \mathcal{A}^{0V} \subseteq \mathcal{R}^{0N} \tag{3.3}$$

and second, the operator $(\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)$ must map each state $|\chi_\nu^\mu(t)\rangle$ onto a finite linear combination $\mathcal{L}_{\mu\nu}$ of the states $\{|\chi_\lambda^\kappa(t)\rangle\}$

$$(\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)|\chi_\nu^\mu(t)\rangle = \mathcal{L}_{\mu\nu}(\{|\chi_\lambda^\kappa(t)\rangle\}) \in [|\chi_\lambda^\kappa(t)\rangle, \lambda = 1, \ldots, L, \kappa = 0, \ldots, K] \tag{3.4}$$

where $L = L(\mu, \nu)$ and $K = K(\mu, \nu)$. The second condition does *not* imply closure of the model space $\mathcal{R}^{MN}$ under the operation $(\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)$, since the linear combination $\mathcal{L}_{\mu\nu}$ may include contributions of higher-order states, i.e. $\kappa > \mu, \lambda > \nu$. The state $(\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)|\chi_\nu^\mu(t)\rangle$ can, however, be written as a finite linear combination of states

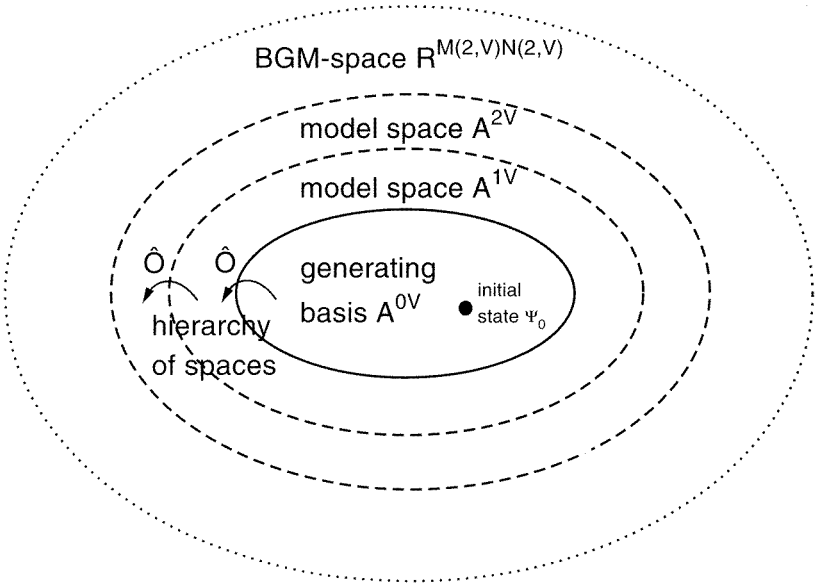

Figure 1. The BGM concept: connection of the BGM space to the generating basis and the corresponding hierarchy of states for a hierarchy of order $U = 2$, illustrating the relation $\mathcal{A}^{0V} \subseteq \mathcal{A}^{1V} \subseteq \mathcal{A}^{2V} \subseteq \mathcal{R}^{M(2,V)N(2,V)}$.

that have the *same structure* as the original state $|\chi_\nu^\mu(t)\rangle$. With conditions (3.3) and (3.4) it follows immediately that

$$\begin{aligned} |\varphi_n^0\rangle &\stackrel{(3.3)}{=} \mathcal{L}(|\chi\rangle) \\ |\varphi_n^1(t)\rangle &= (\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)|\phi_n^0\rangle = (\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)\mathcal{L}(|\chi\rangle) \\ &= \mathcal{L}((\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)|\chi\rangle) \stackrel{3.4}{=} \mathcal{L}(\mathcal{L}(|\chi\rangle)) = \mathcal{L}(|\chi\rangle) \\ &\vdots \\ \mathcal{A}^{UV} &\subseteq \mathcal{R}^{MN} \end{aligned} \tag{3.5}$$

as long as M, N are chosen sufficiently large. The relation of the BGM space $\mathcal{R}^{MN}$ to the hierarchy of states with the corresponding exact model space $\mathcal{A}^{UV}$ and its generating basis $\mathcal{A}^{0V}$ is shown in figure 1 for a hierarchy of states with $U = 2$. This rather low value of U has been chosen to make the figure sufficiently transparent. In practical calculations, the hierarchy order U is usually much larger, taking values around 6–12. Since the model space $\mathcal{A}^{UV}$ is coupled by $\hat{O}(t)$ exclusively to the model space $\mathcal{A}^{(U+1)V}$, the intuitive interpretation of this picture is not misleading.

The statements of this and the previous section apply to any type of time-dependent quantum system and to any kind of time-dependent potential $\hat{V}(t)$ which determines the dynamics of the system, as long as the potential $\hat{V}(t)$ vanishes asymptotically in time. According to the explicit physical system under investigation and the class of time-dependent potentials acting on it, the model space $\mathcal{R}^{MN}$ has to be determined explicitly. For example, the time-dependent quantum system may be a projectile–target–scattering system with the Hamiltonian $\hat{H}_0 = \hat{H}_\mathrm{T}$, $\hat{V}(t) = \hat{V}_\mathrm{P}(t)$ with a passive ion as projectile and an ion, atom or molecule as target, or we can think of a quantum system in a classical laser field with $\hat{H}_0 = \hat{H}_\mathrm{T}$, $\hat{V}(t) = A(t)z$. If investigating a scattering system, the time-dependent potential could be of

the form $\hat{V}_{\mathrm{P}}(t) = \sum_{\kappa=0}^{K} c_\kappa (r_{\mathrm{P}}(t))^{-\kappa}$, including Coulomb and polarization potentials. We could also change our point of view and take the ion as target and a cluster or solid as 'projectile', describing the cluster or the surface of the 'approaching' solid by appropriate potentials $\hat{V}_{\mathrm{P}}(t)$.

In the following section, we discuss the BGM concept for the case of a scattering system with a H-like ion as target under the influence of a time-dependent Coulomb potential due to the incident projectile. We will present an explicit basis set expansion for this system and give a proof of the validity of the conditions (3.3) and (3.4) imposed. In section 5, it is demonstrated that these results can immediately be generalized to the case of a potential of the form $\hat{V}_{\mathrm{P}}(t) = \sum_{\kappa=0}^{K} c_\kappa (r_{\mathrm{P}}(t))^{-\kappa}$. In this way, it is not only possible to address Coulomb systems and systems with a polarization interaction, but also to handle systems with arbitrary potentials that can be expanded in a sum of the above form.

4. The Coulomb interaction

We consider a one-electron interatomic collisional system, where the target is described by the undisturbed Hamiltonian $\hat{H}_0$ in the target system S_{T}, and $\hat{V}(t)$ accounts for the time-dependent influence of the incident projectile. The Hamiltonian can be specified as

$$\begin{aligned}\hat{H}(t) &= \hat{H}_0 + \hat{V}(t) = \hat{H}_{\mathrm{T}} + \hat{V}_{\mathrm{P}}(t) = -\tfrac{1}{2}\Delta + \hat{V}_{\mathrm{T}} + \hat{V}_{\mathrm{P}}(t) \\ &= -\frac{1}{2}\Delta - \frac{Q_{\mathrm{T}}}{r} - \frac{Q_{\mathrm{P}}}{|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{P}}(t)|} \equiv -\frac{1}{2}\Delta - \frac{Q_{\mathrm{T}}}{r} - \frac{Q_{\mathrm{P}}}{r_{\mathrm{P}}(t)}. \end{aligned} \tag{4.1}$$

The motion of the projectile is assumed to follow a straight line

$$\boldsymbol{R}_{\mathrm{P}}(t) = \boldsymbol{b} + \boldsymbol{v}t \tag{4.2}$$

in order to assure that S_{T} is an inertial system. We define the coordinate system of S_{T} in such a way that the scattering plane is given by the (x, z)-plane of S_{T} and the z-axis is parallel to $\boldsymbol{v}$, i.e., $\boldsymbol{R}_{\mathrm{P}}(t) = (b, 0, vt)$, see figure 2.

4.1. Regularization of the Coulomb interaction

In order to calculate the states $|\varphi_v^u(t)\rangle$, derivatives of the Coulomb potential are required. Since the functions $\langle \boldsymbol{r}|\varphi_v^u(t)\rangle$ should remain L^2 Lebesgue-integrable, the Coulomb potentials need to be regularized:

$$\begin{aligned}&\hat{V}_{\mathrm{P}}(t) \to \hat{V}_{\mathrm{P}}(t;\epsilon) = -Q_{\mathrm{P}} W_{\mathrm{P}}(t;\epsilon) \\ &W_{\mathrm{P}}(t;\epsilon) = [(x - R_x(t))^2 + y^2 + (z - R_z(t))^2 + \epsilon^2]^{-1/2} \\ &\qquad\qquad = [r_{\mathrm{P}}(t)^2 + \epsilon^2]^{-1/2} \\ &\hat{V}_{\mathrm{T}} \to \hat{V}_{\mathrm{T}}(\epsilon_{\mathrm{T}}) = -Q_{\mathrm{T}} W_{\mathrm{T}}(\epsilon_{\mathrm{T}}) \\ &W_{\mathrm{T}}(\epsilon_{\mathrm{T}}) = [r^2 + \epsilon_{\mathrm{T}}^2]^{-1/2}. \end{aligned} \tag{4.3}$$

There is no unique way of regularizing Coulomb potentials, but the choice (4.3) is distinguished by the fact that $W_{\mathrm{P}}(t)$ (and analogously W_{T}) can be differentiated to an arbitrary degree and that all derivatives can be expressed in powers of $W_{\mathrm{P}}(t)$ (see appendix A). The regularization $W_{\mathrm{P}}(t;\mu) = r_{\mathrm{P}}(t)^{-1}[1 - \exp(-\mu r_{\mathrm{P}}(t))]$ used in [16] is adequate to ensure the integrability of the wavefunctions $\langle \boldsymbol{r}|\hat{V}^u\varphi_v^0\rangle$, but is inappropriate with respect to the derivatives of the potential needed here.

To be consistent, the regularized Coulomb potentials $\hat{V}_{\mathrm{P}}(t;\epsilon)$ and $\hat{V}_{\mathrm{T}}(\epsilon_{\mathrm{T}})$ are employed both for the generation of the states in the basis and for the solution of the TDSE. The use of the regularization is equivalent to the introduction of a finite size of the projectile and target nuclei. It is consequently expected that the influence of the regularization of the Coulomb

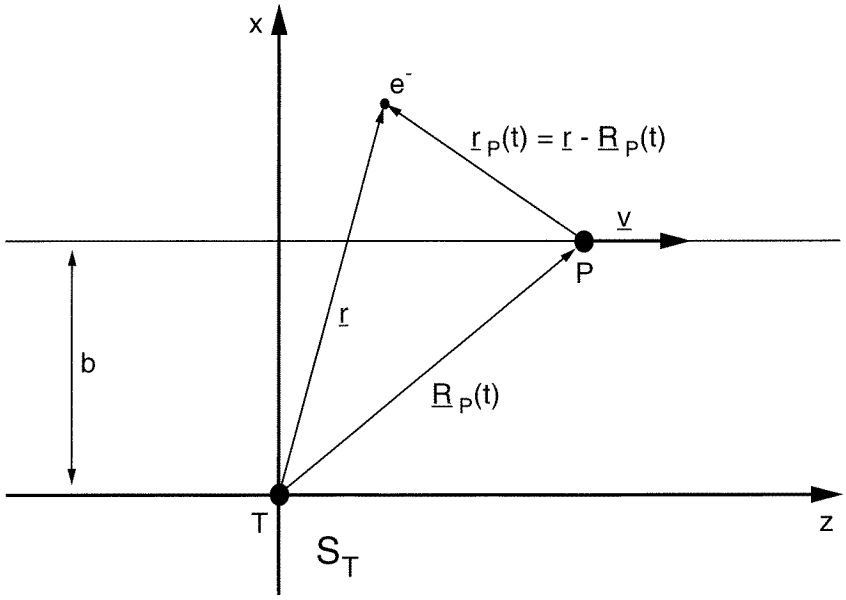

Figure 2. The coordinate system S_T used to describe the scattering of a projectile ion by the H-like target ion.

interaction on the solution of the TDSE is negligible as long as the parameters ϵ and ϵ_T are sufficiently small.

4.2. The hierarchy of states for Coulomb interactions

The basis functions $|\varphi_v^\mu(t)\rangle$ of the first three orders in the hierarchy of states for the regularized Coulomb potential can be derived from (2.8) by means of the relations in appendix A. We use the abbreviation $\tilde{\nabla} \equiv \nabla - \mathrm{i}\dot{\boldsymbol{R}}_P$ to simplify the notation

$$
\begin{aligned}
|\varphi_v^1(t)\rangle &= -Q_P W_P(t)|\varphi_v^0\rangle \\
|\varphi_v^2(t)\rangle &= (-Q_P[\tfrac{3}{2}\epsilon^2 W_P(t)^5 + (\boldsymbol{r}_P(t)\cdot\tilde{\nabla})W_P(t)^3] + Q_P^2 W_P(t)^2)|\varphi_v^0\rangle \\
|\varphi_v^3(t)\rangle &= (Q_P[15\epsilon^2 W_P(t)^7 - \tfrac{105}{4}\epsilon^4 W_P(t)^9 - 15\epsilon^2 W_P(t)^7(\boldsymbol{r}_P(t)\cdot\tilde{\nabla}) \\
&\quad -3W_P(t)^5(\boldsymbol{r}_P(t)\cdot\tilde{\nabla})^2 + W_P(t)^3\tilde{\Delta}] + Q_P Q_T(\boldsymbol{r}_P(t)\cdot\boldsymbol{r})W_P(t)^3 W_T^3 \\
&\quad +Q_P^2[\tfrac{11}{2}\epsilon^2 W_P(t)^6 - W_P(t)^4 + 3W_P(t)^4(\boldsymbol{r}_P(t)\cdot\tilde{\nabla})] - Q_P^3 W_P(t)^3)|\varphi_v^0\rangle.
\end{aligned}
\tag{4.4}
$$

The higher orders can also be derived directly, but—as already seen here—these expressions become very complicated. Fortunately, it is not necessary to know the basis functions in terms of their generating operators explicitly as is shown in the following section.

4.3. Explicit form of the BGM basis set expansion

We have to find states $|\chi_v^\mu(t)\rangle$ whose structure is not changed by the action of the operator $(\hat{H}_0 + \hat{V}(t) - \mathrm{i}\partial_t)$ as required by condition (3.4). This implies that derivatives (e.g. $(r_P(t)\cdot\nabla)$, $\Delta, \ldots$) of $\{\langle\boldsymbol{r}|\chi_v^\mu(t)\rangle\}$ lead to functions of the same type which is a characteristic feature of polynomials and the exponential function. In addition, terms containing the target potential W_T should be completely absorbed by the generating basis $\{\langle\boldsymbol{r}|\chi_v^0\rangle\}$, and terms containing the projectile potential $W_P(t)$ by the BGM basis $\{\langle\boldsymbol{r}|\chi_v^\mu(t)\rangle\}$. In this way we are

systematically led to the following ansatz for a dynamically optimized basis set (we use the conventions $r_{\epsilon_T}^2 \equiv r^2 + \epsilon_T^2$ and $l \equiv h + j + k$)

$$\begin{aligned} \tilde{\chi}^0_{nhjk}(\boldsymbol{r}; \xi, \epsilon_T) &= r_{\epsilon_T}^{n-l-1} x^h y^j z^k \exp(-\xi r_{\epsilon_T}) \\ \tilde{\chi}^\mu_{nhjk}(\boldsymbol{r}, t; \xi, \epsilon_T, \epsilon) &= W_P(t; \epsilon)^\mu \tilde{\chi}^0_{nhjk}(\boldsymbol{r}; \xi, \epsilon_T). \end{aligned} \tag{4.5}$$

Since the physical initial condition is that of an electron on one of two seperated ions, it is favourable not to work with this Cartesian representation, but to introduce an equivalent spherical representation of the basis functions in terms of the spherical harmonics (denoted by Y_l^m in the following) in order to account for the symmetry pattern of the physical process under investigation:

$$\begin{aligned} \chi^0_{nlm}(\boldsymbol{r}; \xi, \epsilon_T) &= r_{\epsilon_T}^{n-1} \exp(-\xi r_{\epsilon_T})(r/r_{\epsilon_T})^l Y_l^m(\theta, \varphi) \\ \chi^\mu_{nlm}(\boldsymbol{r}, t; \xi, \epsilon_T, \epsilon) &= W_P(t; \epsilon)^\mu \chi^0_{nlm}(\boldsymbol{r}; \xi, \epsilon_T) \end{aligned} \tag{4.6}$$

where

$$\begin{aligned} &l, \mu, L, N, M \in \mathcal{N}_0 \qquad m, n, N_z \in \mathcal{Z} \\ &-l \leqslant m \leqslant l \leqslant L \qquad l + N_z < n \leqslant N \\ &N_z \leqslant 0 \leqslant L \leqslant N - 1 \qquad 0 \leqslant \mu \leqslant M. \end{aligned}$$

Apart from the negative powers of r_{ϵ_T} which can enter into equation (4.6) for $n \leqslant l$, the functions χ^0_{nlm} are closely related to spherical Slater-type orbitals. The only difference occurs due to the regularization parameter ϵ_T and vanishes in the limit $\epsilon_T \to 0$. The wavefunctions $\{\chi^\mu_{nlm}(t)\}$ with $\mu > 0$ introduce an *additional* degree of freedom that is *essential* in order to satisfy condition (3.4). The functions $\chi^\mu_{nlm}(t)$ are obviously linearly independent, except for the special case that the origin of the projectile coincides with the origin of the target, which may only happen if the impact parameter b is zero. Because of geometrical reasons, however, this case only contributes to transition amplitudes with weight zero.

In order to prove that the basis set of equation (4.6) is in agreement with conditions (3.3) and (3.4), we first mention that the physically relevant initial condition of the target atom can be expressed in terms of a linear combination of basis functions: this is guaranteed if we assume that the initial wavefunction of the H-like target ion can be expressed as a linear combination of Slater-type orbitals, since Slater-type orbitals can again precisely be approximated by the functions χ^0_{nlm} if ϵ_T is sufficiently small. It is thus possible to define a suitable generating basis $\mathcal{R}^{0N}$.

The difficult part is to show that condition (3.4) is also satisfied. We abbreviate the notation by introducing multi-indices j, k for respective states $|\chi^\mu_{nlm}(t)\rangle$. Since the states $|\chi^\mu_{nlm}(t)\rangle$ form a complete set for *unlimited* values of the indices (n, l, m), the action of the Schrödinger operator $\hat{O}(t)$ on a BGM function can be written as

$$\hat{O}|k(t)\rangle = \sum_{k'} a_{k'}|k'\rangle. \tag{4.7}$$

With respect to (4.7), condition (3.4) requires that the sum should be *finite*. This is equivalent to the requirement that only a finite number of coefficients

$$a_{k'} = \sum_{k''} \langle k'|k''\rangle^{-1} \langle k''|\hat{O}|k\rangle \tag{4.8}$$

may be different from zero. In appendix C it is shown that matrix elements of the form $\langle k''|\hat{O}|k\rangle$ can be readily expressed in terms of a finite sum of overlap matrix elements,

$$\langle k''|\hat{O}|k\rangle = \sum_j^{\text{finite}} b_j \langle k''|j\rangle \qquad j \in \mathcal{I}_k \tag{4.9}$$

where $\mathcal{I}_k$ is a k-dependent set of indices whose maximum number of elements for any k is finite. For the coefficients $a_{k'}$ one thus obtains

$$\begin{aligned} a_{k'} &= \sum_{k''} \langle k'|k''\rangle^{-1} \langle k''|\hat{O}|k\rangle \\ &= \sum_{k''} \sum_{j}^{\text{finite}} b_j \langle k'|k''\rangle^{-1} \langle k''|j\rangle \\ &= b_j \delta_{k'j} \\ &= \begin{cases} b_{k'} & \text{if} \quad k' \in \mathcal{I}_k \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \tag{4.10}$$

Since $\mathcal{I}_k$ is a finite set, only a *finite* number of coefficients $a_{k'}$ are different from zero, q.e.d.

It is interesting to note that the BGM basis set expansion $\{|\chi^{\mu}_{nlm}(t)\rangle\}$ is independent of the velocity v of the projectile and of its charge Q_{P} (see equation (4.6)), although the states $|\varphi^m_n(t)\rangle$ of the hierarchy of states are explicitly dependent on these parameters (see equation (4.4) and appendix A). This is due to the fact that these parameters enter into the equations (C.2) and (C.8) only as constant coefficients. As a consequence, the same BGM basis set may be used to calculate collisions with different values of v and Q_{P}, which is of practical interest.

With respect to practical calculations, we also mention that there is no constraint on the number of different values for ξ entering the BGM basis (4.6). In principle, it is possible to work only with one single value of ξ. It may, however, be favourable to increase the number of ξ-values in order to achieve faster convergence of the BGM basis with respect to the index μ. This especially applies if certain excitation channels become important during the collision because these channels can be included in $\mathcal{R}^{0N}$ using additional values of ξ. Since the choice of the parameters ξ depends on the charge of the target, the BGM basis set expansion becomes implicitly dependent on Q_{T}.

For practical purposes, it is also useful to replace the complex form of the BGM basis by a set of real functions

$$\{Y^m_l(\theta,\varphi), -l \leqslant m \leqslant l\} \rightarrow \{P^m_l(\cos\theta)\cos(m\varphi),\, P^m_l(\cos\theta)\sin(m\varphi), 0 \leqslant m \leqslant l\} \tag{4.11}$$

because of the symmetry introduced by the scattering plane. This symmetry ensures that the gerade part of the basis with $\cos(m\varphi)$ and the ungerade part with $\sin(m\varphi)$ do not mix throughout the collisional process, which simplifies the solution of the TDSE considerably.

We emphasize that—despite the different possible notations of the BGM basis set—the BGM representation *space* is uniquely determined by the BGM conditions (3.3) and (3.4), since these equations fix the boundary conditions both of the stationary and the dynamical part of the BGM representation space. Any additional wavefunction introduced into the BGM basis set either turns out to be redundant or immediately destroys the validity of condition (3.4).

4.4. Matrix elements and the solution of the TDSE

With the BGM basis derived, we now have a suitable tool to solve the TDSE. In the representation space of the BGM basis, the TDSE takes the form of the following coupled channel equations (confer equation (2.6))

$$\begin{aligned} &\mathrm{i}\sum_{\mu=0}^{M}\sum_{nlm} \dot{c}^{\mu}_{nlm}(t)\langle\chi^0_{n'l'm'}|W_{\mathrm{P}}(t)^{\mu'+\mu}|\chi^0_{nlm}\rangle \\ &\qquad = \sum_{\mu=0}^{M}\sum_{nlm} c^{\mu}_{nlm}(t)\langle\chi^0_{n'l'm'}|W_{\mathrm{P}}(t)^{\mu'}(-\tfrac{1}{2}\Delta + \hat{V}_{\mathrm{T}} + \hat{V}_{\mathrm{P}}(t) - \mathrm{i}\partial_t)W_{\mathrm{P}}(t)^{\mu}|\chi^0_{nlm}\rangle \end{aligned} \tag{4.12}$$

where we have used the Schrödinger picture. The matrix elements can be reduced to the overlap matrix S_χ (see appendix C). It is therefore sufficient to calculate only the overlap matrix elements S_χ for every given position R_P of the projectile. The resulting coupled channel equations (4.12) can then be solved by standard methods in a second step. Since the overlap matrix elements are independent of the velocity v and of the projectile charge Q_P, the same set of matrix elements can be used to solve the TDSE of different collisional processes.

In order to get information about physically interesting quantities, e.g. transition amplitudes to characteristic reaction channels, the calculated solution of the TDSE has to be projected on the wavefunctions describing these channels because the BGM basis states do usually not correspond directly with the interesting reaction channels.

5. The basis generator method for potentials $\hat{V}_\mathbf{P} = \sum c_\kappa r_\mathbf{P}^{-\kappa}$

If the projectile potential $\hat{V}_\mathrm{P}(\boldsymbol{r}, t)$ is given as a sum

$$\hat{V}_\mathrm{P}(\boldsymbol{r}, t; \epsilon) = \sum_{\kappa=0}^{K} c_\kappa W(\boldsymbol{r}, t; \epsilon)^\kappa \equiv \sum_{\kappa=0}^{K} c_\kappa \left(\frac{1}{r_{\mathrm{P}_\epsilon}(t)} \right)^\kappa \tag{5.1}$$

of powers of the regularized Coulomb potential $W(t; \epsilon)$ of section 4, we can use the same BGM basis set as given by equation (4.6). The validity of condition (3.3) is guaranteed because the relevant initial condition is independent of the projectile potential $\hat{V}_\mathrm{P}(t)$. The validity of condition (3.4) is a consequence of the fact that the Schrödinger matrix elements can still be reduced to overlap matrix elements in the same way as demonstrated in appendix C. The only difference occurs concerning equation (C.2) because of the different form of $\hat{V}_\mathrm{P}(t)$. As long as $\hat{V}_\mathrm{P}(t)$ is given as a series in powers of $W(t; \epsilon)$, the application of $\hat{V}_\mathrm{P}(t)$ on the BGM states $|\chi^\mu_{nlm}(t)\rangle$ leads again to a linear combination of BGM states

$$\sum_{\kappa=0}^{K} c_\kappa W(t; \epsilon)^\kappa |\chi^\mu_{nlm}(t)\rangle = \sum_{\kappa=0}^{K} c_\kappa |\chi^{\kappa+\mu}_{nlm}(t)\rangle. \tag{5.2}$$

It should, however, be noticed that the number of states needed to describe the exact representation space $\mathcal{A}^{UV}$ to a given order of (U, V) may vary.

Concerning the regularization of the potential $\hat{V}_\mathrm{P}(t)$, it is important to take into account that the singular behaviour near the centre of the force, i.e. $r \approx 0$, of any electrostatic potential is at most proportional to $1/r$. It follows, that an *unregularized* potential $\hat{V}_\mathrm{P}(t)$ becomes unphysical near $r \approx 0$ if any coefficient $c_\kappa \neq 0$ for $\kappa > 1$. With respect to equation (5.1), the regularization of $\hat{V}_\mathrm{P}(t)$ is *essential* to describe a *physically meaningful potential*. If a potential of asymptotic behaviour $1/r^n$ is to be characterized, the appropriate value of ϵ has to be determined simultaneously with the coefficients c_κ, $\kappa \geqslant n$.

In analogy to the argument given in equation (5.2), we may use the BGM basis set (4.6) also in the case of a potential $\hat{V}_\mathrm{T}$ given as a series expansion in $r_{\epsilon_\mathrm{T}}^{-\kappa}$, as long as the physical initial condition according to $\hat{V}_\mathrm{T}$ can be expressed as a linear combination of BGM basis functions. Previous remarks on the meaning of the regularization parameter also apply here.

6. Concluding remarks

We have shown that a hierarchy of dynamically adapted states can be used to systematically define an appropriate basis set for the solution of the TDSE under investigation. This hierarchy is defined in terms of repeated application of the Schrödinger operator on a set of generating states which contains the initial state of the time-dependent quantum system.

In general, this hierarchy of states can only be expressed in terms of a complicated series in operators acting on the generating states. In the case of a Coulomb interaction, another set of states (referred to as the BGM basis) can, however, be constructed, containing the hierarchy of states to a given order exactly. For the BGM basis, *explicit* expressions have been derived. Moreover, the BGM basis is uniquely determined.

The corresponding BGM basis functions are quite similar to Slater-type orbitals: however, additional factors $1/r_{\epsilon_\mathrm{T}}^{|n|}$ and $1/r_{\mathrm{P}_\epsilon}(t)^\mu$ occur. With respect to the completeness relation of the Slater-type orbitals, this seems astonishing at first glance. The completeness relation is of course only valid in the limit of an *infinite* number of functions. Since we are dealing with *finite* basis set expansions, the completeness relation is not applicable. By contrast, the inverse powers of the radial distances in the BGM basis constitute a *resummation* of an infinite number of Slater-type orbitals. In this way, the advantage of the BGM basis set over standard basis set expansions becomes obvious because a better representation of $|\Psi(t)\rangle$ is achieved with a smaller amount of functions. In addition, the maximum inverse powers of the radial distances $r_{\mathrm{P}_\epsilon}(t)$, r_{ϵ_T} occuring in the BGM basis set are *balanced* with respect to the maximum quantum numbers (n, l, m) of the Slater-type part of the basis if the dependency on the indices derived implicitly in appendix C is observed.

Comparing the BGM basis with the basis expansion of [16], which includes the factor $1/r_{\mathrm{P}_\epsilon}(t)^\mu$ but none of the structure $1/r_{\epsilon_\mathrm{T}}^{|n|}$, it becomes obvious that the approximation used in [16] is shown to be adequate for the case of a Coulomb potential. On the other hand, further improvement of the results of practical calculations is to be expected if terms with $1/r_{\epsilon_\mathrm{T}}^{|n|}$ are also taken into consideration.

Another interesting feature of the BGM basis is the fact that these functions account for a *dynamical adaptation* to the time evolution of $|\Psi(t)\rangle$, but have been proven to be explicitly independent of the velocity v of the approaching projectile. The dynamical adaptation of the BGM basis is therefore exclusively determined by the implicit time-dependence of the BGM wavefunctions introduced by the factors $1/r_{\mathrm{P}_\epsilon}(t)^\mu$. In this case, we have demonstrated that the inclusion of *translation factors* in the basis is *not* necessary for an accurate description of the time evolution of the quantum system.

We emphasize that these very appealing features of the BGM basis are due to the consequent restriction of the basis set to describe only the relevant part of Hilbert space. It is clear, that a basis of this form is in general not adequate to represent, e.g., all possible continuum states or all possible charge transfer states of the respective quantum system, since the BGM basis does *not* aim at completeness. However, if a certain continuum state or a particular charge transfer state becomes important for the collisional process in a certain time interval, the BGM basis set expansion covers these segments of Hilbert space *because* they are accessed during the time evolution of the quantum system. Vice versa, if certain states cannot be represented by the BGM basis, then this is due to the fact that they are not relevant to the time evolution of $|\Psi(t)\rangle$. In a rigorous sense, however, these statements hold only if the size of the BGM basis has been adapted to the physical demands of the quantum system under investigation.

In the specification and justification of the explicit BGM basis, the structure of the derivatives of the potentials occuring in the TDSE have turned out to be the crucial point. It can therefore not be expected to find analogous basis set expansions for all kinds of potentials. However, we have shown that the results for the Coulomb interaction can be generalized to potentials that are given in terms of a sum in inverse integer powers of the radial distance, thus including for example the polarization interaction. The BGM concept may, in addition, also be applied to establish suitable basis set expansions for other classes of potentials.

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Appendix A. Derivatives of the regularized Coulomb potential

With the definition of the regularized Coulomb potential

$$W_{\mathrm{P}}(\boldsymbol{r},t;\epsilon)=[r_{\mathrm{P}}(t)^2+\epsilon^2]^{-1/2}\equiv r_{\mathrm{P}_\epsilon}(t)^{-1} \tag{A.1}$$

and the elementary rules

$$\begin{aligned}
&\nabla=(\nabla r_{\mathrm{P}_\epsilon})\frac{\partial}{\partial r_{\mathrm{P}_\epsilon}}=\boldsymbol{r}_{\mathrm{P}}W_{\mathrm{P}}\frac{\partial}{\partial r_{\mathrm{P}_\epsilon}}\\
&\nabla\cdot\boldsymbol{r}_{\mathrm{P}}=3\\
&\partial_t\boldsymbol{r}_{\mathrm{P}}=-\dot{\boldsymbol{R}}_{\mathrm{P}}\\
&\frac{r_{\mathrm{P}}^2}{r_{\mathrm{P}_\epsilon}^2}=1-\epsilon^2W_{\mathrm{P}}^2
\end{aligned} \tag{A.2}$$

all required derivatives can be calculated. Derivatives with respect to spatial coordinates are

$$\begin{aligned}
&\nabla W_{\mathrm{P}}=-\boldsymbol{r}_{\mathrm{P}}W_{\mathrm{P}}^3\\
&\nabla W_{\mathrm{P}}^n=-n\boldsymbol{r}_{\mathrm{P}}W_{\mathrm{P}}^{n+2}\\
&\Delta W_{\mathrm{P}}=-3\epsilon^2W_{\mathrm{P}}^5\\
&\Delta W_{\mathrm{P}}^n=n(n-1)W_{\mathrm{P}}^{n+2}-\epsilon^2n(n+2)W_{\mathrm{P}}^{n+4}\\
&\nabla^3W_{\mathrm{P}}=15\epsilon^2\boldsymbol{r}_{\mathrm{P}}W_{\mathrm{P}}^7.
\end{aligned} \tag{A.3}$$

The derivatives with respect to time have been calculated for a classical straight line motion with $\ddot{\boldsymbol{R}}_{\mathrm{P}}=0$

$$\begin{aligned}
&\partial_tW_{\mathrm{P}}=(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})W_{\mathrm{P}}^3\\
&\partial_tW_{\mathrm{P}}^n=n(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})W_{\mathrm{P}}^{n+2}\\
&\partial_t^2W_{\mathrm{P}}=3(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})^2W_{\mathrm{P}}^5-\dot{\boldsymbol{R}}_{\mathrm{P}}^2W_{\mathrm{P}}^3.
\end{aligned} \tag{A.4}$$

Using equations (A.3) or (A.4), the mixed derivatives with respect to time and spatial coordinates are obtained as

$$\begin{aligned}
&\partial_t\nabla W_{\mathrm{P}}=\dot{\boldsymbol{R}}_{\mathrm{P}}W_{\mathrm{P}}^3-3\boldsymbol{r}_{\mathrm{P}}(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})W_{\mathrm{P}}^5\\
&\partial_t\Delta W_{\mathrm{P}}=-15\epsilon^2(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})W_{\mathrm{P}}^7.
\end{aligned} \tag{A.5}$$

It is clear that analogous relations hold for the derivatives of the regularized Coulomb potential $W_{\mathrm{T}}(\epsilon_{\mathrm{T}})$ with respect to spatial coordinates. One only has to replace $\boldsymbol{r}_{\mathrm{P}}$ by $\boldsymbol{r}$ and ϵ by ϵ_{T} in equation (A.3). Since $W_{\mathrm{T}}(\epsilon_{\mathrm{T}})$ is time-independent, all derivatives of $W_{\mathrm{T}}(\epsilon_{\mathrm{T}})$ with respect to time vanish.

Appendix B. Derivatives of the BGM wavefunctions for $\mu = 0$

For the calculation of matrix elements we have to evaluate $\Delta\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}})$ explicitly. With the definition of the spherical BGM wavefunctions of order $\mu=0$

$$\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}})=r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^lY_l^m(\theta,\varphi) \tag{B.1}$$

the property

$$\Delta Y_l^m(\theta,\varphi) = -\frac{l(l+1)}{r^2} Y_l^m(\theta,\varphi) \tag{B.2}$$

of the spherical harmonics, and the gradient and Laplace operators in spherical coordinates (with $\kappa = \cos\theta$)

$$\begin{aligned} \nabla &= \boldsymbol{e}_r \partial_r - \boldsymbol{e}_\theta \frac{\sqrt{1-\kappa^2}}{r}\partial_\kappa + \boldsymbol{e}_\varphi \frac{1}{r\sqrt{1-\kappa^2}}\partial_\varphi \\ \Delta &= \partial_r^2 + \frac{2}{r}\partial_r + \frac{(1-\kappa^2)}{r^2}\partial_\kappa^2 - \frac{2\kappa}{r^2}\partial_\kappa + \frac{1}{r^2(1-\kappa^2)}\partial_\varphi^2 \end{aligned} \tag{B.3}$$

one immediately sees that

$$\begin{aligned} \Delta\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}}) &= \Delta(r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l) Y_l^m(\kappa,\varphi) \\ &\quad +2\underbrace{\nabla(r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l)}_{\sim \boldsymbol{e}_r}\cdot\underbrace{\nabla(Y_l^m(\kappa,\varphi))}_{\sim \boldsymbol{e}_\theta,\boldsymbol{e}_\varphi} \\ &\quad +r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l \Delta(Y_l^m(\kappa,\varphi)) \\ &= \left(\partial_r^2 + \frac{2}{r}\partial_r\right)(r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l) Y_l^m(\kappa,\varphi) \\ &\quad -l(l+1)r_{\epsilon_{\mathrm{T}}}^{n-3}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^{l-2} Y_l^m(\kappa,\varphi). \end{aligned} \tag{B.4}$$

The calculation of the radial derivatives is straightforward and one finally arrives at

$$\begin{aligned} \Delta\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}}) &= -(n-l-1)(n-l-3)\epsilon_{\mathrm{T}}^2\chi^0_{(n-4)lm} + 2(n-l-\tfrac{3}{2})\epsilon_{\mathrm{T}}^2\xi\chi^0_{(n-3)lm} \\ &\quad +[n(n-1)-l(l+1)-\epsilon_{\mathrm{T}}^2\xi^2]\chi^0_{(n-2)lm} - 2n\xi\chi^0_{(n-1)lm} + \xi^2\chi^0_{nlm}. \end{aligned} \tag{B.5}$$

Neglecting terms of order ϵ_{T}^2, relation (B.5) reduces to the well known eigenvalue equation

$$\left(-\frac{1}{2}\Delta - \frac{l(l+1)}{2r^2} + V_{n\xi}^{\mathrm{STO}}\right)\psi_{nlm}^{\mathrm{STO}} = -\frac{1}{2}\xi^2\psi_{nlm}^{\mathrm{STO}} \tag{B.6}$$

of the Slater-type orbitals

$$\psi_{nlm}^{\mathrm{STO}}(\boldsymbol{r};\xi) = r^{n-1}\exp(-\xi r)Y_l^m(\theta,\varphi) \tag{B.7}$$

with the potential

$$V_{n\xi}^{\mathrm{STO}} \equiv \frac{n(n-1)}{2r^2} - \frac{n\xi}{r}. \tag{B.8}$$

Appendix C. Evaluation of matrix elements

In order to solve the TDSE (4.12), the following matrix elements are needed:

$$\begin{aligned} S_\chi^{(n'l'm')(nlm)(\mu'+\mu)} &\equiv \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu}|\chi^0_{nlm}\rangle \\ M_{\mathrm{S}}^{(n'l'm')\mu'(nlm)\mu} &\equiv \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'}\hat{O}\,W_{\mathrm{P}}^{\mu}|\chi^0_{nlm}\rangle \\ &= \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'}(-\tfrac{1}{2}\Delta + \hat{V}_{\mathrm{T}} + \hat{V}_{\mathrm{P}} - \mathrm{i}\partial_t)W_{\mathrm{P}}^{\mu}|\chi^0_{nlm}\rangle. \end{aligned} \tag{C.1}$$

With the aid of appendices A and B, the Schrödinger matrix M_{S} can be readily expressed in terms of the overlap matrix S_χ between BGM states. The potential matrix elements

$$\begin{aligned} \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu}\hat{V}_{\mathrm{T}}|\chi^0_{nlm}\rangle &= -Q_{\mathrm{T}}S_\chi^{(n'l'm')((n-1)lm)(\mu'+\mu)} \\ \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu}\ \hat{V}_{\mathrm{P}}|\chi^0_{nlm}\rangle &= -Q_{\mathrm{P}}S_\chi^{(n'l'm')(nlm)(\mu'+\mu+1)} \end{aligned} \tag{C.2}$$

can be evaluated without further difficulty. Considering the stationarity of the functions χ^0_{nlm} and using equation (A.4), the matrix elements including derivatives with respect to time can be transformed into

$$\begin{aligned}\langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'}(-\mathrm{i}\partial_t)W_{\mathrm{P}}^{\mu}|\chi^0_{nlm}\rangle &= -\mathrm{i}\mu\langle\chi^0_{n'l'm'}|(\dot{\boldsymbol{R}}_{\mathrm{P}}\cdot\boldsymbol{r}_{\mathrm{P}})W_{\mathrm{P}}^{\mu'+\mu+2}|\chi^0_{nlm}\rangle \\ &= -\mathrm{i}\mu\langle\chi^0_{n'l'm'}|v(z-vt)W_{\mathrm{P}}^{\mu'+\mu+2}|\chi^0_{nlm}\rangle \end{aligned} \tag{C.3}$$

for a straight line movement of the projectile. The evaluation of $z\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}})$ is more involved. With the abbreviation $\kappa\equiv\cos\theta$ we first rewrite

$$\begin{aligned} z\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}}) &= r\kappa r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l Y_l^m(\kappa,\varphi) \\ &= r\kappa\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}r_{\epsilon_{\mathrm{T}}}^{n-1}\exp(-\xi r_{\epsilon_{\mathrm{T}}})(r/r_{\epsilon_{\mathrm{T}}})^l P_l^m(\kappa)\mathrm{e}^{\mathrm{i}m\varphi}. \end{aligned} \tag{C.4}$$

Employing the well known relation

$$(2l+1)\kappa P_l^m(\kappa) = (l-m+1)P_{l+1}^m(\kappa)+(l+m)P_{l-1}^m(\kappa) \tag{C.5}$$

which holds both for positive and negative values of m if the convention

$$P_l^{-m}(\kappa) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\kappa) \tag{C.6}$$

is used, and taking into account that $r^2 = r_{\epsilon_{\mathrm{T}}}^2-\epsilon_{\mathrm{T}}^2$, one obtains

$$\begin{aligned} z\chi^0_{nlm}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}}) &= \sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}}\chi^0_{(n+1)(l+1)m}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}}) \\ &+\sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}(\chi^0_{(n+1)(l-1)m}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}})-\epsilon_{\mathrm{T}}^2\chi^0_{(n-1)(l-1)m}(\boldsymbol{r};\xi,\epsilon_{\mathrm{T}})). \end{aligned} \tag{C.7}$$

Together with equation (C.3) this finally yields

$$\begin{aligned} \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'}(-\mathrm{i}\partial_t)W_{\mathrm{P}}^{\mu}|\chi^0_{nlm}\rangle &= \mathrm{i}\mu(v^2t)S_\chi^{(n'l'm')(nlm)(\mu'+\mu+2)} \\ &-\mathrm{i}\mu v\sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}}S_\chi^{(n'l'm')((n+1)(l+1)m)(\mu'+\mu+2)} \\ &-\mathrm{i}\mu v\sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}(S_\chi^{(n'l'm')((n+1)(l-1)m)(\mu'+\mu+2)} \\ &-\epsilon_{\mathrm{T}}^2 S_\chi^{(n'l'm')((n-1)(l-1)m)(\mu'+\mu+2)}). \end{aligned} \tag{C.8}$$

According to [16], the matrix representation of the Laplace operator can be reduced to

$$\begin{aligned} \langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'}(-\tfrac{1}{2}\Delta)W_{\mathrm{P}}^{\mu}|\chi^0_{nlm}\rangle &= -\frac{\mu}{2(\mu'+\mu)}\langle\Delta\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu}|\chi^0_{nlm}\rangle \\ &-\frac{\mu'}{2(\mu'+\mu)}\langle\chi^0_{n'l'm}|W_{\mathrm{P}}^{\mu'+\mu}|\Delta\chi^0_{nlm}\rangle+\frac{1}{2}\mu'\mu\langle\chi^0_{n'l'm'}|(\nabla W_{\mathrm{P}})^2W_{\mathrm{P}}^{\mu'+\mu-2}|\chi^0_{nlm}\rangle. \end{aligned} \tag{C.9}$$

The last term of the right-hand side of equation (C.9)

$$\begin{aligned} \tfrac{1}{2}\mu'\mu\langle\chi^0_{n'l'm'}|(\nabla W_{\mathrm{P}})^2W_{\mathrm{P}}^{\mu'+\mu-2}|\chi^0_{nlm}\rangle &= \tfrac{1}{2}\mu'\mu\langle\chi^0_{n'l'm'}|r_{\mathrm{P}}^2W_{\mathrm{P}}^{\mu'+\mu+4}|\chi^0_{nlm}\rangle \\ &= \tfrac{1}{2}\mu'\mu\langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu+2}|\chi^0_{nlm}\rangle-\tfrac{1}{2}\mu'\mu\epsilon^2\langle\chi^0_{n'l'm'}|W_{\mathrm{P}}^{\mu'+\mu+4}|\chi^0_{nlm}\rangle \\ &= \tfrac{1}{2}\mu'\mu S_\chi^{(n'l'm')(nlm)(\mu'+\mu+2)}-\tfrac{1}{2}\mu'\mu\epsilon^2S_\chi^{(n'l'm')(nlm)(\mu'+\mu+4)} \end{aligned} \tag{C.10}$$

is again expressed in terms of the overlap matrix only. Since we have

$$\langle\chi^0_{(n'-1)l'm'}|W_{\rm P}^{\mu'+\mu}|\chi^0_{nlm}\rangle = \langle\chi^0_{n'l'm'}|W_{\rm P}^{\mu'+\mu}|\chi^0_{(n-1)lm}\rangle \tag{C.11}$$

the first two terms of the right-hand side of equation (C.9) can be evaluated with the aid of equation (B.5):

$$\begin{aligned}
&-\frac{\mu}{2(\mu'+\mu)}\langle\Delta\chi^0_{n'l'm'}|W_{\rm P}^{\mu'+\mu}|\chi^0_{nlm}\rangle - \frac{\mu'}{2(\mu'+\mu)}\langle\chi^0_{n'l'm}|W_{\rm P}^{\mu'+\mu}|\Delta\chi^0_{nlm}\rangle \\
&\quad = -\frac{1}{2(\mu'+\mu)}((\mu'+\mu)\xi^2 S_\chi^{(n'l'm')(nlm)(\mu'+\mu)} \\
&\qquad -2(n\mu'+n'\mu)\xi S_\chi^{(n'l'm')((n-1)lm)(\mu'+\mu)} \\
&\qquad +\{[n(n-1)-l(l+1)]\mu'+[n'(n'-1)-l'(l'+1)]\mu\}S_\chi^{(n'l'm')((n-2)lm)(\mu'+\mu)} \\
&\qquad -(\mu'+\mu)\epsilon_{\rm T}^2\xi^2 S_\chi^{(n'l'm')((n-2)lm)(\mu'+\mu)} \\
&\qquad +2[(n-l-\tfrac{3}{2})\mu'+(n'-l'-\tfrac{3}{2})\mu]\epsilon_{\rm T}^2 S_\chi^{(n'l'm')((n-3)lm)(\mu'+\mu)} \\
&\qquad -[(n-l-1)(n-l-3)\mu'+(n'-l'-1)(n'-l'-3)\mu] \\
&\qquad \times\epsilon_{\rm T}^2 S_\chi^{(n'l'm')((n-4)lm)(\mu'+\mu)}).
\end{aligned} \tag{C.12}$$

In this way, all relevant matrix elements have been reduced to simple overlap matrix elements. We emphasize that only terms with the structure $S_\chi^{(n'l'm')(\ldots)\cdot}$ contribute. In a slightly different notation, this important feature is expressed in equation (4.9). The above calculations also demonstrate that the number of contributing overlap matrix elements is always the same, except for the special case that some of the contributions vanish as their coefficients become zero. These two facts are the key to the proof of the validity of the BGM basis as shown in section 4.3.

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