

## CHAPTER

# 1 INTRODUCTION TO ATOM-LASER DYNAMICS

Any attempted theoretical description of atom–laser dynamics is built on a number of assumptions that are guided either by the need to obtain a computationally tractable problem or by the pertaining experimental conditions. The atom or molecule is considered as being isolated and distorted only by an electromagnetic (EM) pulse lasting for a few femtoseconds or less. Of no concern here are the technicalities of how these pulses are produced, but their properties are of interest; these pulses may lie in the long-wavelength regime (e.g., visible window) or could be of shorter-wavelength radiation delivered from free-electron lasers (FELs) or high-harmonic generation (HHG) sources. For events occurring on the femtosecond timescale, the theoretical analysis does not include the spontaneous decay of the excited states, so when a calculation of the population of an excited state is reported, it means just after the external pulse has vanished. Obviously, after some time the excited states will decay to lower states by spontaneously emitting radiation.<sup>1</sup>

Generally, interaction with a lower-intensity field is treated perturbatively; for long-wavelength pulses, the amplitude  $\mathcal{E}_0$  of the applied electric field is small relative to that of the Coulombic (static) electric field in atomic hydrogen, i.e.,  $\mathcal{E}_0 \ll 5.142 \times 10^9$  V/cm. However, this is not generally the case when the pulse's frequency spectrum is higher than the visible window or the pulse becomes very short. Typically, for pulses of higher intensities, perturbation conditions eventually become invalid, and any calculation becomes questionable regarding whether it reflects actual events. Higher intensity is not the only reason for a perturbative calculation to break down (e.g., resonance conditions); when this happens, direct solution of the time-dependent Schrödinger equation (TDSE) should be considered.

The inevitable outcome of ultra-short laser–atom interactions is ionization with large probability,<sup>2</sup> meaning that the atom will very likely lose one or more electrons; as a general rule, the higher the intensity, the larger the ionization probability. Depending on the pulse and the atomic or molecular structure, the excitation probability could also be nonnegligible, which means that by the end of the interaction, the system may be found in one of its excited states (i.e., by performing an energy measurement just after).

From the perspective of quantum mechanics (QM), the presence of the pulse creates a nonstationary time-dependent quantum state that can be described in either (i) the energy representation by tracing

<sup>1</sup> Actually, this process is not so spontaneous because it is induced by the vacuum EM field.

<sup>2</sup> Of course, with an upper limit of unity.

the expansion coefficients  $C_a(t)$  on the atomic Hamiltonian's eigenbasis  $|\phi_a\rangle$ , i.e.,

$$|\psi(t)\rangle = \sum_a C_a(t) |\phi_a\rangle, \quad (1.1)$$

or (ii) the position representation by directly calculating the time-dependent wavefunction  $\psi(\mathbf{x}, t) = \langle \mathbf{x} | \psi \rangle$ .

In what follows, the TDSE in the context of atom–laser dynamics is discussed. The discussion is restricted to single-active electron (SAE) dynamics, in which approximation the probability of multi-electron excitation/ionization is negligibly small.

After establishing the TDSE and solving in lowest order to the electric field, we discuss briefly a more general approach involving time-dependent perturbation theory (TDPT). These introductory presentations allow the introduction of various concepts and relevant terminology.

## 1.1 TDSE OF ATOMS IN LASER FIELDS

We want to examine the effects on an atomic system due to its coupling with a *pulsed* EM field. The atom is affected such that its state *during* and *after* the interaction with the pulse differs from that *before*, in that any *one* of its electrons practically changes its spatiotemporal properties (the SAE approximation). We express the situation in this way because in principle an electron inside an atom cannot exist by “itself” and can only approximately be considered as an individual quantum object on its own; according to QM, the atom is described by a wavefunction containing the coordinates of all electrons in a purely democratic fashion. Of course, such conceptual and practical problems are not present in hydrogenic atomic systems, e.g., hydrogen (H), singly ionized helium ( $\text{He}^+$ ), doubly ionized lithium ( $\text{Li}^{+2}$ ), etc.

Consider the atomic Hamiltonian  $\hat{h}_0$  subject to a time-dependent EM potential  $\hat{V}(\mathbf{x}, \mathbf{p}; t)$ . Let the atomic system's *state* be  $|\psi(t)\rangle$  and the corresponding (position) *wavefunction* be  $\psi(\mathbf{x}, t) = \langle \mathbf{x} | \psi(t) \rangle$ , then its causal time evolution law is the TDSE, i.e.,

$$i \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = \left[ \hat{h}_0(\mathbf{x}, \mathbf{p}) + \hat{V}(\mathbf{x}, \mathbf{p}, t) \right] \psi(\mathbf{x}, t) \quad \psi_0(\mathbf{x}) \equiv \psi(\mathbf{x}, t_0), \quad (1.2)$$

where  $\psi(\mathbf{x}, t_0)$  is the atomic state at time  $t_0$ . Because the TDSE includes the first derivative of the state with respect to time, knowledge of the state at a fixed time  $t_0$  is required. The assumption is that  $\hat{h}_0$  does not depend explicitly on time. We also assume a transient interaction in the sense that

$$\hat{V}(\mathbf{x}, \mathbf{p}; t) \xrightarrow{t \rightarrow \pm\infty} 0. \quad (1.3)$$

Some preparatory clarifications are required before we work out solutions of the TDSE; for this, we examine briefly the nature of the two terms on the right-hand side (RHS) of the TDSE.

**The atomic Hamiltonian**  $\hat{h}_0$ . We model the position representation of the atomic Hamiltonian by

$$\hat{h}_0(\mathbf{x}, \mathbf{p}) = -\frac{\nabla^2}{2} + V(\mathbf{x}). \quad (1.4)$$

For now, we assume that we can solve the *field-free* TDSE, i.e.,

$$\left( i\frac{\partial}{\partial t} - \hat{h}_0 \right) \phi_a(\mathbf{x}, t) = 0 \quad \rightarrow \quad (\hat{h}_0 - \epsilon_a)\phi_a(\mathbf{x}) = 0, \quad (1.5)$$

where  $\phi_a(\mathbf{x}) = e^{-i\epsilon_a(t-t_0)}$  and the index  $a$  indicates proper quantum numbers to define fully the system's eigenstates and eigenenergies. In accord with QM principles, these states are orthogonal to each other and form a complete basis for any state in which the atom can be found. However, their normalization is less clear cut: on one hand, when they are spatially bound, they exist at only discrete negative energies ( $\epsilon_a < 0$ ) and can be normalized trivially to unity; on the other hand, when they are spatially unbound, they exist for all continuous positive energies ( $\epsilon_a > 0$ ) and generally cannot be normalized to unity.<sup>3</sup> The former eigenstates decay exponentially in the radial direction (*bound* states) and are denoted as  $\phi_b(\mathbf{x}) = \langle \mathbf{x} | \phi_b \rangle$ ; meanwhile, the latter unbound eigenstates oscillate radially and are denoted as  $\phi_c(\mathbf{x}) = \langle \mathbf{x} | \phi_c \rangle$  (often called *free*, *ionization*, *continuum*, or *scattering* states, among other names). We can quantify further the nature of the  $\hat{h}_0$  eigenstates based on their asymptotic boundary conditions (BCs):<sup>4</sup>

$$\phi_b(\mathbf{x}) \xrightarrow{r \rightarrow \infty} e^{-\sqrt{-\epsilon_b}r}, \quad \epsilon_b < 0, \quad (1.6)$$

$$\phi_c(\mathbf{x}) \xrightarrow{r \rightarrow \infty} A_c \sin(k_c r + \Delta_c), \quad k_c = \sqrt{2\epsilon_c}, \quad \epsilon_c > 0, \quad (1.7)$$

where  $\mathbf{x} = (r, \theta, \phi)$ . Formally, we may (temporarily) hide the issue of normalization for the unbound eigenstates if instead of using the position representation, we express the orthonormalization and completeness properties in abstract form, i.e.,

$$\langle \phi_a | \phi_b \rangle = \delta_{ab}, \quad \sum_a \int |\phi_a\rangle \langle \phi_a| = \mathbb{1}. \quad (1.8)$$

The combined symbol for sum and integration emphasizes that  $a$  takes integer and real values due to the bound and unbound spectrum, respectively.

**The interaction term and the pulse,  $\mathbf{A}(\mathbf{r}, t)$ .** One particular form of the interaction potential in the so-called *Coulomb-gauge*<sup>5</sup> potential ( $\nabla \cdot \mathbf{A} = 0$ ) is given (in atomic units) by

$$V(\mathbf{x}, \mathbf{p}, t) = \frac{1}{c} \mathbf{A}(y, t) \cdot \mathbf{p} = \hat{z} \frac{1}{c} A(y, t) \hat{p}_z, \quad (1.9)$$

<sup>3</sup> For single-electron systems, the energy point that separates the bound and unbound states of the system is conventionally set to zero, but obviously any other value is equally acceptable if preferred; this is because only energy differences are physically meaningful.

<sup>4</sup> The unbound BCs are derived in Chap. 6; see (6.62).

<sup>5</sup> One more form that is used very frequently is the *length-gauge* interaction  $V(\mathbf{x}, \mathbf{p}, t) = \mathbf{x} \cdot \mathbf{E}(\mathbf{x}, t)$ . It has its own merits as well, which will be discussed in later chapters.

with the pulse described classically via its potential  $A(y, t)$  propagating along the  $y$  axis and linearly polarized along the  $z$  axis (see Fig. 9.1 in Chap. 9):

$$A(y, t) = A_0(t) \cos(k_L y - \omega_L t + \phi_L), \quad (1.10)$$

where  $A_0(t)$  is the pulse's *envelope*, and  $\omega_L$  and  $\phi_L$  are the field's central carrier frequency and phase, respectively, both of which are assumed to be *time-independent*.<sup>6</sup> In the *Coulomb-gauge*, the electric field is given by  $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} / c$ . The function  $A_0(t) = A_0 f(t/\tau)$  is slowly varying on the time scale of the field's period  $T_L = 2\pi/\omega_L$  and ensures that the EM field vanishes in the remote past and future ( $t \rightarrow \pm\infty$ ); the exact manner in which this happens may matter, especially in resonant ionization conditions. A good approximation is to take  $A_0(t)$  to have a Gaussian shape [ $f(t) = e^{-t^2/\tau_L^2}$ ], but for convenience other forms may also be used, such as Lorentzian [ $f(t) = e^{-|t|/\tau_L}$ ], secant [ $f(t) = 1/\text{sech}(t/\tau_L)$ ], or the *Hann window* function  $f(t) = \sin^2(\pi t/\tau_L)$ , with the latter being a particularly practical pulse for calculations because of its sharp end time points at  $t = 0, \tau_L$ .

## 1.2 TDSE IN THE ENERGY BASIS

We now proceed to cast the TDSE in a form that is amenable to more-practical solutions. For this, using the completeness relation of (1.8), we write

$$|\psi(t)\rangle = \sum_a |\phi_a\rangle \langle \phi_a | \psi(t)\rangle = \sum_a C_a(t) |\phi_a\rangle.$$

Clearly, because  $|\phi_a\rangle$  are Hamiltonian's eigenstates, the set of the  $C_a(t)$  amplitudes represents the atomic state in the energy basis. For reasons of later convenience, we make the connection with the wavefunction by taking the projection to the position basis  $\psi(\mathbf{x}, t) = \langle \mathbf{x} | \psi(t)\rangle$ , i.e.,

$$\psi(\mathbf{x}, t) = \sum_a C_a(t) \phi_a(\mathbf{x}). \quad (1.11)$$

Also, from  $\phi_a(\mathbf{x}) = \langle \mathbf{x} | \phi_a\rangle$  and  $\int d\mathbf{x} |\mathbf{x}\rangle \langle \mathbf{x}| = \mathbb{1}$ , we have the following practical expression for the amplitudes  $C_a(t)$ :

$$C_a(t) = \langle \phi_a | \psi(\mathbf{x}, t)\rangle = \int d\mathbf{x} \phi_a^*(\mathbf{x}) \psi(\mathbf{x}, t). \quad (1.12)$$

Considering the classification of the  $\phi_a(\mathbf{x})$  states as bound and unbound states as in (1.6) and (1.7), we can also write<sup>7</sup>

$$\psi(\mathbf{x}, t) = \sum_{\epsilon_b < 0} C_b(t) \phi_b(\mathbf{x}) + \sum_{\epsilon_c > 0} d\epsilon_c C_c(t) \phi_c(\mathbf{x}). \quad (1.13)$$

<sup>6</sup> This is not an essential requirement for our discussion because with some extra effort the case of a time-dependent phase  $\phi_L$  can also be incorporated.

<sup>7</sup> Note that as well as the energy observable, the atomic states can also be classified in terms of other quantum observables (which may be discrete or continuous valued), such as according to their angular momentum and spin state (in addition to their energy).

Now, given that  $\phi_a(\mathbf{x})$  are assumed known, the interest shifts to calculating  $C_a(t)$ , which is a single-variable problem.<sup>8</sup> Our next task is to establish the system of ordinary differential equations (ODEs) governing the  $C_a(t)$  coefficients. Substituting the time-dependent wavefunction (1.11) into both sides of the TDSE (1.2), we have

$$i\frac{\partial}{\partial t} \sum_{a'} C_{a'}(t)\phi_{a'}(\mathbf{x}) = \left[ \hat{h}_0 + \hat{V}(\mathbf{x}, t) \right] \sum_{a'} C_{a'}(t)\phi_{a'}(\mathbf{x}),$$

and multiplying the latter equation from the left by  $\phi_a^*(\mathbf{x})$  followed by spatial integration (thus projecting), we obtain

$$\sum_{a'} i\dot{C}_{a'}(t)\langle\phi_a|\phi_{a'}\rangle = \sum_{a'} C_{a'}(t) \left( \langle\phi_a|\hat{h}_0(\mathbf{x})|\phi_{a'}\rangle + \langle\phi_a|\hat{V}(\mathbf{x}, t)|\phi_{a'}\rangle \right),$$

where the spatial and time dependences are shown explicitly for clarity. From the orthonormalization condition of the Hamiltonian basis, we have  $\langle\phi_a|\phi_{a'}\rangle = \delta_{aa'}$ , and from the eigenvalue equation  $\hat{h}_0\phi_{a'} = \epsilon_{a'}\phi_{a'}$  we obtain  $\langle\phi_a|\hat{h}_0|\phi_{a'}\rangle = \epsilon_{a'}\delta_{aa'}$ . Finally, the summations on the left-hand side (LHS) and the first term on the RHS are reduced to just one (*diagonal* in matrix parlance) term,  $a = a'$ :

$$i\frac{d}{dt}C_a(t) = \epsilon_a C_a(t) + \sum_{a'} \hat{V}_{aa'}(t)C_{a'}(t), \quad (1.14)$$

where

$$V_{aa'}(t) = \langle\phi_a|\hat{V}(\mathbf{x}, t)|\phi_{a'}\rangle = \int d\mathbf{x} \phi_a^*(\mathbf{x})V(\mathbf{x}, t)\phi_{a'}(\mathbf{x}). \quad (1.15)$$

The spatial integration involved in the interaction matrix elements has eliminated all spatial variables from the resulting equations. If the atomic system is initially in some state  $\psi_0(\mathbf{x})$ , then the values of  $C_a(t_0)$  are determined by

$$C_a(t_0) = \langle\psi_0(\mathbf{x})|\psi(\mathbf{x}, t_0)\rangle,$$

where  $t_0$  must be a time at which the external field is zero. In the frequently encountered case in which the initial state is one of the system's eigenstates, say the  $\phi'_a(\mathbf{x})$  eigenstate, quite generally  $C_{a'}(t_0) = e^{i\eta}$ , with  $\eta$  an arbitrary real-valued number and all the other coefficients vanishing. If the atomic state is not specially prepared under the conditions discussed in the opening section, then the initial state is the ground state. The value of  $\eta$  has no physical significance (and is set to zero) unless the initial state is a degenerate one, in which case a consistent formulation for the temporal development of a quantum state is obtained through the density-operator formalism.

We must comment explicitly on the physical significance of the time-dependent amplitudes  $C_a(t)$ ; these coefficients have a definite physical meaning only when the interaction term is not present, i.e.,  $V(\mathbf{x}, t) = 0$ . Provided here is a heuristic interpretation of the  $C_a(t)$  amplitudes in a spectral basis

<sup>8</sup> The expansion in (1.11) is a *separation-of-variables* method, very frequently used to reduce multidimensional partial differential equations to simpler ones of lower dimensions. In the QM context, it appears to have been used first by Dirac as early as 1927.

expansion as probability distributions: in the remote past when the interaction term is not present, the system is in any one of the eigenstates of  $\hat{H}_0$  (or in any combination of them, a wavepacket), and then the interaction term switches on and changes the system's Hamiltonian, causing a time development of the wavefunction beyond the field-free time evolution (based on  $\hat{H}_0$  alone); in the far future, the interaction vanishes and the system is eventually found in a state that can be represented as a wavepacket, again expressed as eigenstates of  $\hat{H}_0$  alone. The probability distribution among the various eigenstates at time  $t$  can be found as the transition probability from the initial state  $\psi(\mathbf{x}, t_0)$  to another state  $\phi_a(\mathbf{x})$  at time  $t$ ; at time  $t$ , the initial state has evolved to  $\psi(\mathbf{x}, t)$ , so the probability amplitude can be obtained by projecting the state  $\phi_a(\mathbf{x})$  on the system's state  $\psi(\mathbf{x}, t)$  of (1.1), i.e.,

$$P_a(t, t_0) = |C_a(t)|^2 = |\langle \phi_a(\mathbf{x}) | \psi(\mathbf{x}, t) \rangle|^2. \quad (1.16)$$

In summary, we interpret  $|C_a(t \rightarrow \infty)|^2$  as the probability of an energy measurement of the field-free atom to give the  $E_a$  value; of course, by QM principles, just after this measurement the atom evolves in the state  $|\phi_a\rangle$ . The situation is less clear when the pulse is on: the atom is intimately coupled with the field, and their values depend on the chosen form of the interaction potential. For example, the time evolution of  $C_a(t)$  is different if we choose the *Coulomb-gauge* or the *length-gauge* form (see Chap. 8) to express the interaction potential, so their physical meaning must be different in these two gauges. Nevertheless, their values must be the same each time the interaction potential vanishes, even if it is during the pulse.

Up to this point, we have considered no essential approximation in terms of the strength and duration of the external potential, and therefore the resultant ODE formulation of the TDSE on the  $\hat{h}_0$  basis provides the means for the complete solution of the interaction problem. Simple inspection of the ODEs reveals that the only dynamical quantities of interest are the eigenenergies  $E_a$  and the transition matrix elements  $V_{aa'}(t)$ ; both are known provided the field-free eigenvalue Hamiltonian problem has been solved. Then, using the TDSE ODEs, the  $C_a(t)$  are calculated at the end of the pulse, and from there via (1.12), the  $\psi(\mathbf{x}, t)$  or any other quantity of interest can also be calculated. This is generally the normal sequence of steps to solve the TDSE in the energy basis (or *spectral* basis). As a quick comment, the system's time-dependent wavefunction need not be expanded in its eigenstates basis but rather in any other complete basis (e.g., discrete-variable-representation basis, B-splines polynomial basis, etc.).

### 1.3 FIRST- AND SECOND-ORDER APPROXIMATIONS

At this point, any applicable computational algorithm is relevant, and which one is most suitable depends on the particular problem; nevertheless, all the candidate algorithms should have some general properties. Now we want to study the excitation/ionization processes triggered by the interaction between the atom and the laser pulse assuming a laser field that is not too strong. First, we assume that the atom is initially in one of its bound eigenstates (let us call it  $\psi(\mathbf{x}, t_0) = \phi_0(\mathbf{x})$ ); the initial time  $t_0$  is dictated by the specific choice of pulse, and it is chosen such that the pulse is not present

[so  $A_0(t) = 0$ ]. Second, we write down the TDSE ODEs (1.14) for the  $C_0(t)$  and the remaining states separately:

$$i\dot{C}_a(t) = \epsilon_a C_a(t) + V_{a0}(t)C_0(t) + \sum_{a' \neq 0} V_{aa'}(t)C_{a'}(t), \quad (1.17)$$

$$i\dot{C}_0(t) = \epsilon_0 C_0(t) + \sum_{a'} V_{0a'}(t)C_{a'}(t). \quad (1.18)$$

We take the diagonal elements for the interaction potential as being zero from the outset,<sup>9</sup> i.e.,  $V_{aa} = 0$ . Next, we formally integrate the equation for  $C_0(t)$ :

$$C_0(t) = C_0(t_0)e^{-i\epsilon_0(t-t_0)} - i \sum_{a'} \int_{t_0}^t dt_1 V_{0a'}(t_1)e^{-i\epsilon_0(t-t_1)} C_{a'}(t_1). \quad (1.19)$$

Let us now estimate the  $C_0(t)$  dependence on the field's strength and duration by examining the second term in the RHS of the above equation; assuming the interaction term has a duration  $\tau_0$ , if the magnitude of the interaction term is  $V_0$ , then this term scales as  $\sim \tau_0 V_0$ . Similarly, integration of (1.17) provides the  $C_a(t)$  amplitudes as

$$C_a(t) = C_a(t_0)e^{-i\epsilon_a(t-t_0)} - i \int_{t_0}^t dt_1 V_{a0}(t_1)e^{-i\epsilon_a(t-t_1)} C_0(t_1) - i \sum_{a' \neq 0} \int_{t_0}^t dt_1 V_{aa'}(t_1)e^{-i\epsilon_a(t-t_1)} C_{a'}(t_1). \quad (1.20)$$

The above solutions for  $C_0(t)$  and  $C_a(t)$  are only formal because the RHSs of these equations include the values of  $C_0(t_1)$  and  $C_{a'}(t_1)$  at times less than  $t$ ; at first sight, this looks like a dead end. However, there is a way out if we try to solve these equations perturbatively, i.e., using (1.19) and (1.20) to express  $C_0(t_1)$  and  $C_{a'}(t_1)$  ( $t_1 < t$ ) and then replacing these expressions back in (1.19) and (1.20).<sup>10</sup> This replacement generates extra terms, which in turn requires the aforementioned coefficients  $C_a(t)$  and  $C_0(t)$  at even earlier times, which looks like the dead end has just shifted to earlier times; however, what is gained here is that *these subsequent terms require the interaction at earlier times and at higher order*, and provided that  $\tau_0 V_0 \ll 1$ , they are less important to forming the full values of the amplitude coefficients  $C_a(t)$  and  $C_0(t)$ .

We call the approximation *first order* when the interaction term is linear in  $V_0\tau_0$ , *second order* when the interaction term is proportional to  $(V_0\tau_0)^2$ , and so on. Here, we will be calculating the transition amplitude and the time evolution of the wavefunction to the first two orders. Therefore, for the given physical situation, we take  $C_0(t_0) = 1$  and  $C_a(t_0) = 0$ . Now, upon substituting  $C_0(t_1)$  and  $C_{a'}(t_1)$  in the

<sup>9</sup> Which is generally the case for the atom–laser interaction potential, but if it is not, then it can be incorporated in the diagonal part of the ODEs by redefining  $\epsilon_a \rightarrow \epsilon_a + V_{aa}(t)$ . In fact, perturbative solutions of order higher than one also entail such an extended definition of the energy of state *inside the field*, known as ac-Stark shifts.

<sup>10</sup> Alternatively, these values can also be substituted into the corresponding ODEs (1.18) and (1.17).

expression for  $C_a(t)$ , (1.20), we obtain

$$C_a(t) = -i \int_{t_0}^t dt_1 V_{a0}(t_1) e^{-i\epsilon_a \tau_1} \left( e^{-i\epsilon_0 \tau_{10}} - i \sum_{a'} \int_{t_0}^{t_1} dt_2 V_{0a'}(t_2) e^{-i\epsilon_0 \tau_{12}} C_{a'}(t_2) \right) \\ - i \sum_{a' \neq 0} \int_{t_0}^t dt_1 V_{aa'}(t_1) e^{-i\epsilon_a \tau_1} \left( -i \int_{t_0}^{t_1} dt_2 V_{a'0}(t_2) e^{-i\epsilon_{a'} \tau_{12}} C_0(t_2) \right. \\ \left. - i \sum_{a'' \neq 0} \int_{t_0}^{t_1} dt_2 V_{a'a''}(t_2) e^{-i\epsilon_{a''} \tau_{12}} C_{a''}(t_2) \right),$$

where  $t_{ij} \equiv t_i - t_j$ ,  $\tau_j = t - t_j$  were introduced. By separating this expansion in terms of the power order of the interaction potential,  $\sim V, V^2$ , four terms appear as

$$C_a(t) = -i \int_{t_0}^t dt_1 e^{-i\epsilon_a \tau_1} V_{a0}(t_1) e^{-i\epsilon_0 \tau_{10}} \\ - \sum_{a'} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{-i\epsilon_a \tau_1} V_{a0}(t_1) V_{0a'}(t_2) e^{-i\epsilon_0 \tau_{12}} C_{a'}(t_2) \\ - \sum_{a' \neq 0} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{-i\epsilon_a \tau_1} V_{aa'}(t_1) V_{a'0}(t_2) e^{-i\epsilon_{a'} \tau_{12}} C_0(t_2) \\ - \sum_{a' \neq 0} \sum_{a'' \neq 0} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 V_{aa'}(t_1) e^{-i\epsilon_a \tau_1} V_{a'a''}(t_2) e^{-i\epsilon_{a''} \tau_{12}} C_{a''}(t_2). \quad (1.21)$$

We can see now that the first-order approximation is obtained if we ignore the last three terms, which are of the order of  $\sim (\tau_0 V_0)^2$ . From the last three terms, the dominant term is the one containing the initial state coefficient  $C_0(t_2)$  because the assumption is that at all times  $|C_a(t)|^2 \ll |C_0(t_2)|^2$ , or in other words, the excitation/ionization is always a small fraction relative to the population in the initial state. With all that in mind, the first- and second-order approximations are given by

$$C_a^{(1)}(t) = -i \int_{t_0}^t dt_1 e^{-i\epsilon_a(t-t_1)} V_{a0}(t_1) e^{-i\epsilon_0(t_1-t_0)}, \quad (1.22)$$

$$C_a^{(2)}(t) \simeq - \sum_{a' \neq 0} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{-i\epsilon_a \tau_1} V_{aa'}(t_1) V_{a'0}(t_2) e^{-i\epsilon_{a'} \tau_{12}} C_0(t_2). \quad (1.23)$$

In the expression for  $C_a^{(2)}(t)$ , note the symbol  $\simeq$  in contrast to the equality symbol for  $C_a^{(1)}(t)$ : this is to emphasize that we have ignored the two terms containing  $C_{a'}(t_2)$  and  $C_{a''}(t_2)$ , which is equivalent to having set them to zero.

Following the same procedure for the initial state coefficient  $C_0(t)$ , so replacing  $C_{a'}(t_1)$  [by evaluating (1.20) at time  $t_1$ ] in (1.19), we obtain



$$C_0(t) = C_0(t_0)e^{-i\epsilon_0\tau_0} - i\sum_{a'} \int_{t_0}^t dt_1 V_{0a'}(t_1)e^{-i\epsilon_0\tau_1} \left( C_{a'}(t_0)e^{-i\epsilon_a\tau_{10}} - i\int_{t_0}^{t_1} dt_2 V_{a'0}(t_2)e^{-i\epsilon_{a'}\tau_{12}} C_0(t_2) - i\sum_{a'' \neq 0} \int_{t_0}^{t_1} dt_2 V_{a'a''}(t_2)e^{-i\epsilon_{a'}\tau_{12}} C_{a''}(t_2) \right). \quad (1.24)$$

Now we can work on this iterative expression a bit more and separate the various term, as we did for  $C_a(t)$ , and then we may set  $C_0(t) \simeq 1$  and  $C_a(t) \simeq 0$  if we wish. At this point, we leave this task to the interested reader and bypass these intermediate steps to present only the final expression for the  $C_0(t)$  coefficient:

$$C_0^{(1)}(t) = e^{-i\epsilon_0(t-t_0)} C_0(t_0), \quad (1.25)$$

$$C_0^{(2)}(t) \simeq -\sum_{a'} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{-i\epsilon_0\tau_1} V_{0a'}(t_1) V_{a'0}(t_2) e^{-i\epsilon_{a'}\tau_{12}} C_0(t_2). \quad (1.26)$$

As earlier, the terms with  $C_a(t)$  have been ignored relative to the  $C_0(t)$  values. With these last equations, we have the first- and second-order perturbative terms for the  $C_0(t)$  and  $C_a(t)$  amplitudes. In the presence of weak fields where very low ionization is observed, we may also set  $C_0(t) \simeq 1$  and proceed with the evaluation of the terms provided the relevant transition amplitudes and energies are known; based on these equations in Chap. 9, we develop a weak-field photoionization theory.

## 1.4 ac-STARK SHIFT AND IONIZATION WIDTH

Using the previous results, we take the opportunity to introduce two very common quantities related with the photoionization process, generally known as the *ac-Stark shift* and *ionization width* of an atomic state. To simplify the discussion, we assume an electric field that is varying very slowly relative to the field's oscillation period  $2\pi/\omega_L$ ,<sup>11</sup> and with a duration and amplitude such that no significant depletion of the ground state has occurred by the end of the interaction.

Under these conditions, we may rely on the perturbative expression for the initial state amplitude, given by the sum of (1.25) and (1.26) as

$$C_0(t) \simeq C_0^{(1)}(t) + C_0^{(2)}(t).$$

For subsequent manipulations, it is convenient to multiply both sides of this equation by  $e^{i\epsilon_0 t}$  and perform some formal manipulations that include replacing  $\tau_1 = t - t_1$  and  $\tau_{12} = t_1 - t_2$  to arrive at

$$e^{i\epsilon_0 t} C_0(t) = e^{i\epsilon_0 t_0} C_0(t_0) - \sum_{a'} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{-i(\epsilon_0 - \epsilon_{a'})(t_1 - t_2)} V_{0a'}(t_1) V_{a'0}(t_2) e^{i\epsilon_0 t_2} C_0(t_2).$$

Now we can define  $u_j(t) = e^{i\epsilon_0 t_j} C_0(t_j)$ ,  $j = t, t_0, t_2$  and work with these transformed amplitudes; the conclusions are unaffected by this change of basis (known as the interaction picture) because

<sup>11</sup> For even more simplicity, the reader may even assume a square pulse for which  $E(t) = E_0 \cos \omega_L t$ .

$|u_0(t)|^2 = |C_0(t)|^2$ . Taking advantage of the fact that the oscillating factor in the integral depends on the  $\tau = t_1 - t_2$  difference, we change the innermost integration variable:

$$u_0(t) = u_0(t_0) - \sum_{a'} \int_{t_0}^t dt_1 \int_0^{t_1-t_0} d\tau e^{-i(\epsilon_0 - \epsilon_{a'})\tau} V_{0a'}(t_1) V_{a'0}(t_1 - \tau) u_0(t_1 - \tau).$$

Next, we do two things: (i) we take the derivative with respect to  $t$ , which eliminates the first integral; (ii) we proceed with the following approximation:

$$V_{a'0}(t_1 - \tau) u_0(t_1 - \tau) \simeq V_{a'0}(t_1) u_0(t_1). \quad (1.27)$$

Actually, this replacement involves two approximations, and some discussion is called for here. First, we recall (1.9) to write (setting  $\phi_L = 0$  for simplicity)

$$V_{ab}(t) = \mu_{ab}^v \frac{A_0(t)}{c} \frac{1}{2} (e^{i\omega_L t} + e^{-i\omega_L t}) = \mu_{ab}^v \frac{A_0(t)}{c} \frac{1}{2} e^{i\omega_L t} (1 + e^{-2i\omega_L t}),$$

where  $\mu_{ab}^v = \langle \phi_a | \hat{P} | \phi_b \rangle$  is the momentum matrix element (velocity gauge) between two eigenstates of the system's Hamiltonian. For the last expression, upon integration over a time interval containing many cycles of oscillation ( $\tau \gg T_L$ ), the second (highly oscillating) term  $e^{2i\omega_L t}$  sums to a much smaller value than the unity term, so we ignore it;<sup>12</sup> this is known as the *rotating-wave approximation* (RWA).

The remaining time-dependent term is the envelope, which by definition is slowly varying relative to the field's oscillation period  $T_L = 2\pi/\omega_L$ ; more specifically, thinking of a Taylor expansion

$$A_0(t - \tau) \simeq A_0(t) - \tau \dot{A}_0(t) - \frac{1}{2} \tau^2 \ddot{A}_0(t) + \dots,$$

the slowly varying approximation (SVA) keeps only the first term provided that

$$\tau \dot{A}_0(t) \ll A_0(t). \quad (1.28)$$

The time scale of variation of the pulse's envelope is the pulse's duration  $\tau_L$ ; this allows us to replace  $|\dot{A}_0(t)|$  with  $|A_0(t)/\tau_L|$ . So, from the above SVA condition and the RWA condition, we end up with the following requirements for the assumed  $\tau$ :

$$T_L \ll \tau \ll \tau_L. \quad (1.29)$$

Therefore, in what follows, time derivatives should be understood to involve *coarse-grained* time intervals of the order of  $\tau$  and slowly varying quantities.

Having clarified the conditions required for the SVA and RWA, we now apply (1.27) and arrive at

$$\frac{d}{dt} u_0(t) = -u_0(t) \sum_{a'} |V_{0a'}(t)|^2 \int_0^{t-t_0} d\tau e^{i(\epsilon_0 + \omega_L - \epsilon_{a'})\tau},$$

where we have changed  $t_1$  to  $t$  to drop the useless index. At this point, we must account for the fact that the ionization states of the atom are actually continuous in the index  $a'$  rather than discrete, so we

<sup>12</sup> To see this, just integrate in time, i.e.,  $\int_0^\tau dt (1 + e^{-2i\omega_L t})$  with  $\tau \gg 2\pi/\omega_L$ . The negative and positive values of the oscillating term combine to almost complete cancellation.

change  $a'$  to  $\epsilon$  and the summation over the index  $a'$  becomes an integral. Moreover, for more insight, we factorize the dependence of  $V(t)$  as

$$V_{a'0}(t) \rightarrow V_{\epsilon 0}(t) = \frac{1}{c} \mu_{\epsilon 0}^v \frac{A_0(t)}{2}.$$

With all these changes, we obtain

$$\dot{u}_0(t) = \frac{|A_0(t)|^2}{4c^2} u_0(t) \int_0^\infty d\epsilon |\mu_{\epsilon 0}^v|^2 \int_0^{t-t_0} d\tau e^{i(\epsilon_0 + \omega_L - \epsilon)\tau} = \frac{|A_0(t)|^2}{4c^2} \mathcal{F}_\epsilon(t) u_0(t).$$

The integral over time is half the  $\delta$ -Dirac function, and sufficiently large time is expressed formally as (Cohen, 1987)

$$\Delta_\epsilon = \epsilon_0 + \omega_L - \epsilon \rightarrow \int_0^{t-t_0} d\tau e^{i\Delta_\epsilon \tau} = \mathcal{P}\left(\frac{t}{\Delta_\epsilon}\right) + \pi \delta(\Delta_\epsilon), \quad \Delta_\epsilon \tau \gg 1.$$

Then the integral over the energy continuum gives

$$\mathcal{F}_\epsilon(t) = i \left( \mathcal{P} \int_0^\infty d\epsilon \frac{|\mu_{\epsilon 0}^v|^2}{\Delta_\epsilon} - i\pi |\bar{\mu}_{\epsilon 0}^v|^2 \right).$$

The time evolution of the amplitude of the initial state takes the form

$$i\dot{u}_0(t) = \left[ s_0(t) - i \frac{\gamma_0(t)}{2} \right] u_0(t), \quad (1.30)$$

with the *ionization width*  $\gamma_0(t)$  and the *ac-Stark shift*  $s_0(t)$  defined as

$$\gamma_0(t) = 2\pi |\mu_{\epsilon_L 0}^v|^2 \frac{|A_0(t)|^2}{4c^2}, \quad (1.31)$$

$$s_0(t) = \left( \mathcal{P} \int_0^\infty d\epsilon \frac{|\mu_{\epsilon 0}^v|^2}{\epsilon_0 + \omega_L - \epsilon} \right) \frac{|A_0(t)|^2}{4c^2}. \quad (1.32)$$

The principal-value integral  $\mathcal{P} \int d\epsilon |\mu_{\epsilon 0}^v|^2 / (\epsilon_0 + \omega - \epsilon)$  excludes the “resonance” energy  $\epsilon_L = \epsilon_0 + \omega_L$  from the integration range, while the momentum matrix element is evaluated on this resonance energy  $\epsilon_L$ :

$$\mu_{\epsilon_L 0}^v = \mu_{\epsilon 0}^v \Big|_{\epsilon = \epsilon_0 + \omega_L}.$$

The radiation coupling of the ground state with the continuum states is now represented entirely by  $s_0(t)$  and  $\gamma_0(t)$ , which give rise to an energy shift and an ionization rate, respectively. The coarse-grained time evolution for the ground state  $u_0(t)$  is now effectively *independent* on the  $u_a(t)$  states.

**Square pulse**,  $A(t) = A_0/2 = \text{const}$ . This case is highly justified for a very long pulse (containing many cycles) with very short ramp-on and ramp-off durations. Taking  $t_0 = 0$ , the initial (discrete) state time evolution is given by

$$u_0(t) = e^{-i(s_0 - i\frac{\gamma_0}{2})t} \rightarrow |u_0(t)|^2 = e^{-\gamma_0 t}, \quad (1.33)$$

and the ionization width is given by

$$\gamma_0 = 2\pi |\mu_{\epsilon_1 0}^v|^2 \frac{|A_0|^2}{4c^2}. \quad (1.34)$$

**Length gauge.** We have derived these expressions using the *momentum matrix elements*, but similar expressions may be derived using dipole matrix elements  $\mu_{ab} = \langle a | \hat{X} | b \rangle$ ; a quick derivation is presented here. Because  $A(t) = A_0(t) \cos \omega_L t$  and  $E(t) = -\dot{A}/c$ , for the electric field we have

$$E(t) = \frac{\omega_L}{c} A_0(t) \left( \sin \omega_L t - \frac{\dot{A}_0}{A_0 \omega_L} \cos \omega_L t \right) \simeq \frac{\omega_L}{c} A_0(t) \sin \omega_L t + \mathcal{O}(T_L/\tau_L).$$

The second term is ignored on the basis of the coarse-grained assumption (1.29) because

$$\left| \frac{\dot{A}_0}{\omega_L A_0} \right| \sim \frac{(A_0/\tau_L)}{A_0(2\pi/T_L)} = \frac{T_L}{2\pi \tau_L} \ll 1.$$

From this expression, we take the electric field's envelope as  $E_0(t) = \omega_L A_0(t)/c$ , which if replaced in (1.34) gives

$$\gamma_0 = 2\pi \frac{|\mu_{\epsilon_1 0}^v|^2}{\omega_L^2} \frac{|E_0(t)|^2}{4}.$$

We require an expression that contains the dipole matrix elements; for this, we use the QM definition of the momentum operator  $\mathcal{P} \equiv i[\hat{h}_0, \hat{X}]$  to obtain

$$\langle \phi_a | \mathcal{P} | \phi_b \rangle = \langle \phi_a | \hat{h}_0 \hat{X} - \hat{X} \hat{h}_0 | \phi_b \rangle = (\epsilon_a - \epsilon_b) \langle \phi_a | \hat{X} | \phi_b \rangle.$$

In our particular case in which  $\epsilon_L = \epsilon_0 + \omega_L$ , we have

$$\mu_{ab}^v = (\epsilon_a - \epsilon_b) \mu_{ab}^l \quad \rightarrow \quad \mu_{\epsilon_1 0}^v = (\epsilon_1 - \epsilon_0) \mu_{\epsilon_1 0}^l = \omega_L \mu_{\epsilon_1 0}^l.$$

Now using the last relation  $\bar{\mu}_{ab}^l = \omega_{ab} \bar{\mu}_{\epsilon_0}^v$ , we give the expressions for the ac-Stark shift and the ionization width in terms of the dipole matrix elements (length gauge):

$$\gamma_0(t) = 2\pi |\mu_{\epsilon_1 0}^l|^2 \frac{|E_0(t)|^2}{4}, \quad (1.35)$$

$$s_0(t) = \left( \mathcal{P} \int_0^\infty d\epsilon \frac{|\mu_{\epsilon_0}^l|^2}{\epsilon_0 + \omega_L - \epsilon} \right) \frac{|E_0(t)|^2}{4}. \quad (1.36)$$

**Photoionization cross section.** This is the right place to introduce the single-photon cross section in terms of the ionization width of the initial state. Staying with the length-gauge form, for the time average of the field's intensity in terms of its electric field, we have  $\mathcal{I}_0(t) = c|E_0(t)|/8\pi$ ; replacing this value in (1.35), we obtain

$$\gamma_0(t) = \frac{4\pi^2}{c} \omega_L |\mu_{\epsilon_1 0}^l|^2 \frac{\mathcal{I}_0(t)}{\omega_L} = \sigma_1^l(\omega_L) \mathcal{F}_0(t). \quad (1.37)$$

The quantity  $\sigma_1(\omega_L)$  is known as the *single-photon photoionization cross section*, and  $\mathcal{F}_0(t)$  is the field's *photon flux*. This perturbative factorization of the ionization width and the concept of ionization

cross section (expressed in square centimeters in SI units) is used to characterize the response of an atomic system independently of the field's intensity (although not independently of its polarization state and frequency content); the physical justification for this improves with more field cycles and lower intensity, i.e., keeping the ratio  $\mathcal{I}_0/\omega_L$  low.

Finally, without giving the details, it is a straightforward exercise to derive the same expression in the velocity gauge (this task is left to the reader):

$$\gamma_0(t) = \frac{4\pi^2}{\omega_L c} |\mu_{\epsilon_L 0}^v|^2 \frac{\mathcal{I}_0(t)}{\omega_L} = \sigma_1^v(\omega_L) \mathcal{F}_0(t). \quad (1.38)$$

**Schrödinger picture.** It is interesting to recover the time evolution of the  $C_0(t)$  amplitude. Substituting  $e^{i\epsilon_0 t} C_0(t)$  into (1.30) gives

$$i\dot{C}_0(t) = \left[ \epsilon_0 + s_0(t) - i\frac{\gamma_0(t)}{2} \right] C_0(t), \quad (1.39)$$

so we can generally state the following. *Any atomic state in the presence of an external laser field changes its energy and is unstable; in the limit of low intensity, these correspond to the ac-Stark shift and the ionization width.*

## 1.5 BASICS OF TIME-DEPENDENT PERTURBATION THEORY

In this section, we develop a more rigorous method for calculating the time evolution of a QM state including higher orders of the external (time-dependent) potential. This is a more systematic and general method, and it is an indispensable computational tool when calculating quantities for which perturbative conditions apply (the Hamiltonian can split into parts that differ considerably in their contributions to the system's time evolution); this is what TDPT is about.

More specifically, consider the physical situation discussed in (1.2)–(1.5) but with the difference that now we will be using the Hilbert abstract vector formulation of QM to represent states and operators. So, we make the replacement

$$i\frac{d}{dt}|\psi(t)\rangle = [\hat{H}_0 + \hat{V}(t)]|\psi(t)\rangle \quad (1.40)$$

and keep only the time dependence visible. We assume that the reader is familiar with this more general QM formulation; otherwise, advice from more-advanced texts in general QM theory is recommended (Messiah, 1999; and Weinberg, 2015). If required, soon after establishing the key formulas of TDPT, it is easy to return to the position basis to recover the space–time description. Also, by using this formulation, we are no longer restricted to systems described by just one particle; the formulation applies equally well to multiparticle systems.

The success of any perturbation method—time-dependent or not—is based on its ability to converge quickly with respect to the perturbation parameter. Therefore, it is important for a likely fast-converged

perturbation series to choose a split of the system's total Hamiltonian such that  $\hat{V}(t)$  actually represents a small fraction of it; so in  $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ , the main actor should necessarily be the  $\hat{H}_0$  part. However, the split should be such that the eigenvalue problem of  $\hat{H}_0$  is understood easily and with the minimum of approximations. In summary, for a perturbation method, we require (ideally) the following:

- a split of the total Hamiltonian as  $\hat{H} = \hat{H}_0 + \hat{V}$ , with
- the spectrum of  $\hat{H}_0$  known fully (eigenvalues and eigenstates  $E_a, \phi_a$ );
- for the magnitudes  $|\hat{V}| \ll |\hat{H}_0|$ , so  $\hat{V}$  is a *perturbation* to  $\hat{H}_0$ .

To take full advantage of the *unperturbed* part of the spectrum (field-free), we perform a basis transformation to the so-called *interaction or Dirac picture* (IP) [in contrast to the more familiar Schrödinger (SP) and Heisenberg (HP) pictures], which is defined by

$$\tilde{\psi}(t) \equiv e^{i\hat{H}_0 t} |\psi(t)\rangle. \quad (1.41)$$

One may wonder how the exponential of an operator (or more generally a function of an operator) should be understood and calculated practically; the conventional approach is to employ a definition via an expansion in a series. For example, the Taylor theorem can be used to represent the action of the exponential operator in an arbitrary wavefunction as

$$e^{\alpha\hat{H}_0} |\psi\rangle = \sum_n \frac{(\alpha\hat{H}_0)^n}{n!} |\psi\rangle = (\mathbb{1} + \alpha\hat{H}_0 + \frac{1}{2!}(\alpha\hat{H}_0)(\alpha\hat{H}_0) + \dots) |\psi\rangle. \quad (1.42)$$

Whether this particular Taylor expansion is practical is less important at this moment; several other methods can be used to calculate this exponential, which in passing is a matter of major importance in practical calculations across most scientific disciplines.<sup>13</sup> More formally now, this transformation eliminates the time dependence of the  $\hat{H}_0$  eigenstates. For example, if  $\phi_a$  is a *time-independent* solution of the  $\hat{H}_0$  eigenvalue equation in the SP equation (1.5), then its time evolution in the SP and IP is

$$|\phi_a(t)\rangle = e^{-i\hat{H}_0 t} |\phi_a\rangle \quad \rightarrow \quad \tilde{\phi}_a(t) = e^{i\hat{H}_0 t} e^{-i\hat{H}_0 t} |\phi_a\rangle = |\phi_a\rangle,$$

which means that in the IP, a field-free problem involves no time evolution at all for the  $H_0$  eigenstates. Soon, we will show that any time evolution that may occur is due exclusively to the interaction potential  $\tilde{V}(t)$ , now expressed in the IP. Regarding the latter, it is easy to see that the operators in the IP are related to those in the SP by

$$\tilde{Q}(t) = e^{i\hat{H}_0 t} \hat{Q}(t) e^{-i\hat{H}_0 t} \quad \Leftrightarrow \quad \iota \frac{d\tilde{Q}}{dt} = [\tilde{Q}, \hat{H}_0] + \frac{\partial \tilde{Q}}{\partial t}. \quad (1.43)$$

The only exception to this is the potential-free Hamiltonian  $\hat{H}_0$  itself (and any other operator commuting with  $\hat{H}_0$ ). So if  $\hat{O}$  commutes with  $\hat{H}_0$ , i.e.,  $\hat{O}F(\hat{H}_0) = F(\hat{H}_0)\hat{O}$ , where  $F$  is an arbitrary function,

<sup>13</sup> This practical aspect is discussed in Chap. 4.

then we have

$$\tilde{O}(t) = e^{i\hat{H}_0 t} \hat{O}(t) e^{-i\hat{H}_0 t} = e^{i\hat{H}_0 t} e^{-i\hat{H}_0 t} \hat{O}(t) = \hat{O}(t).$$

Note that in the IP, constant operators in the SP ( $\hat{O}(t) \equiv \hat{O}$ ) do obtain time dependence as concluded from (1.43). We can now turn the SP TDSE into its IP counterpart by substituting (1.41) in (1.40) to give

$$i \frac{\partial}{\partial t} (e^{-i\hat{H}_0 t} \tilde{\psi}(t)) = [\hat{H}_0 + \hat{V}(t)] e^{-i\hat{H}_0 t} \tilde{\psi}(t).$$

Performing the time derivative in the LHS followed by multiplying both sides from the left with  $e^{i\hat{H}_0 t}$  and using  $e^{i\hat{H}_0 t} \hat{H}_0 e^{-i\hat{H}_0 t}$ , we obtain

$$\hat{H}_0 \tilde{\psi}(t) + e^{-i\hat{H}_0 t} i \frac{\partial}{\partial t} \tilde{\psi}(t) = \hat{H}_0 \tilde{\psi}(t) + e^{i\hat{H}_0 t} \hat{V}(t) e^{-i\hat{H}_0 t} \tilde{\psi}(t),$$

whereupon we end up with the IP TDSE:

$$i \frac{\partial}{\partial t} \tilde{\psi}(t) = \tilde{V}(t) \tilde{\psi}(t), \quad (1.44)$$

$$\tilde{V}(t) = e^{i\hat{H}_0 t} \hat{V}(t) e^{-i\hat{H}_0 t}. \quad (1.45)$$

The initial condition for  $\tilde{\psi}_0$  is obtained from (1.41) at  $t = t_0$ . The IP TDSE has the same form as that of the SP TDSE (1.40) but with  $\hat{H}(t)$  replaced by  $\tilde{V}(t)$  and  $|\psi(t)\rangle$  replaced by  $\tilde{\psi}(t)$ .

### 1.5.1 Iterative Dyson series

We now develop a solution of the IP TDSE by integrating it with respect to time by brute force, which involves repeated time integrations of its RHS as follows:

$$\tilde{\psi}(t) = \tilde{\psi}_0 - i \int_{t_0}^t dt_1 \tilde{V}(t_1) \tilde{\psi}(t_1). \quad (1.46)$$

The above expression gives  $\tilde{\psi}(t)$  based on its values at all earlier times  $t_0 < t_1 < t$ , which as it stands is void of use. To arrive at a practical formula, we must eliminate  $\tilde{\psi}(t_1)$  from the integrand. For this, we evaluate (1.46) at  $t_1$  to obtain  $\tilde{\psi}(t_1) = \tilde{\psi}_0 - i \int_{t_0}^{t_1} dt_2 \tilde{V}(t_2) \tilde{\psi}(t_2)$  and then use it to replace  $\tilde{\psi}(t_1)$  in (1.46) to obtain

$$\tilde{\psi}(t) = \tilde{\psi}_0 - i \int_{t_0}^t dt_1 \tilde{V}(t_1) \tilde{\psi}_0 + (-i)^2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \tilde{V}(t_1) \tilde{V}(t_2) \tilde{\psi}(t_2).$$

The second term can be evaluated given  $\tilde{\psi}_0$  and  $\tilde{V}(t_1)$ ; in this way, we have moved the calculational problem to the third term because the values of  $\tilde{\psi}(t_2)$  are required in the restricted time interval of  $t_0 \leq t_2 \leq t_1 \leq t$ . However,  $t_1$  itself takes values from  $t_0$  to  $t$ , thus making  $t_2$  also take values from  $t_0$  to  $t$  at times at which  $\tilde{V}(t)$  is nonvanishing. This means that if the interaction  $\tilde{V}(t)$  has maximum amplitude  $V_0$  and a duration of order  $\tau_0$ , then the second term is first order in  $V_0 \tau_0$  and the third term is second order in  $(V_0 \tau_0)^2$ . Of crucial importance here is ensuring that in the integration of the third term, only

products  $\tilde{V}(t_1)\tilde{V}(t_2)$  with  $t_2 < t_1$  are taken into account, because generally  $\tilde{V}(t_1)\tilde{V}(t_2) \neq \tilde{V}(t_2)\tilde{V}(t_1)$ . This is achieved straightforwardly if one assumes a specific representation in which  $\tilde{V}(t)$  is generally represented as a matrix, say  $\mathbf{V}_1$  when evaluated at  $t_1$  and  $\mathbf{V}_2$  when evaluated at  $t_2$ ; for matrices, it is known that  $\mathbf{V}_1\mathbf{V}_2 \neq \mathbf{V}_2\mathbf{V}_1$ .

There is nothing forbidding us from following the same procedure for a third time, which generates a fourth term of third order in  $(V_0\tau_0)^3$  involving an integrand  $\tilde{V}(t_1)\tilde{V}(t_2)\tilde{V}(t_3)$ , again taking care to evaluate only quantities with  $0 < t_3 < t_2 < t_1$ . We can repeat this procedure as many times as we please, and as such we obtain the following order- $n$  expansion for the time-dependent wavefunction:

$$\tilde{\psi}(t) = e^{\int_0^t dt \tilde{V}(t)} \tilde{\psi}_0 = \left( \mathbb{1} + \tilde{V}^{(1)}(t, t_0) + \tilde{V}^{(2)}(t, t_0) + \dots \right) \tilde{\psi}_0 \quad (1.47)$$

$$V^{(n)}(t, t_0) = (-i)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \tilde{V}(t_1)\tilde{V}(t_2)\dots\tilde{V}(t_n), \quad (1.48)$$

where *Dyson's chronological operator*  $e^{\int_0^t dt \tilde{V}(t)}$  is defined by its action in the state  $\tilde{\psi}_0$ ; note that this is identical to the exponential operators only when the matrix representations of  $\tilde{V}(t)$  commute at different times, in the sense discussed previously.

To summarize, this form of the solution contains increasing powers of  $V_0\tau_0$ , and provided that these are less than unity, then the terms in the sum are of decreasing order, resulting in a practically legitimate perturbative expansion. The breaking of the total Hamiltonian into two parts  $\hat{H}_0 + \hat{V}$  associates most of the dynamics with the  $\hat{H}_0$  part, assuming that it is taken into account exactly, thereby allowing us to truncate the higher terms of the above IP infinite expansion on the basis that they do not contribute significantly to the “remaining” dynamics. Therefore, in designing a perturbative method,  $|\hat{V}_0| \ll |\hat{H}_0|$  is the first step for a proper application of the infinite expansion, with the second step being to ensure that successive terms become smaller (e.g.,  $V_0\tau_0 \ll 1$ ). An application of the first-order perturbation theory is presented in Chap. 9 for a space–time description of the photoionization process of an atomic system subjected to a (weak) pulsed laser field.

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