The role of anharmonicity and coupling in quantum computing based on vibrational qubits

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Abstract. We analyse the effects of molecular characteristics on the structure of global quantum gates and the complexity of the resulting mechanisms systematically with the goal of rating a molecule’s suitability for molecular quantum computing. One decisive property of a molecular vibration is the anharmonicity and in an extension to multimode systems the mode coupling has to be taken into account additionally. In a parametrized two-dimensional model system, we tune these characteristic properties and explore their effects on quantum gates. We find that the interplay of the anharmonicity and the coupling is of prime importance and leads to two basic control mechanisms for all systems. The features of quantum gate laser fields are explained with characteristic transition frequencies, determined by the molecular parameters, and the limits to obtain simple structures are identified.

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1. Introduction

Quantum computation represents a major topic in the field of quantum information theory. Pioneering theoretical and experimental work has been performed in interdisciplinary branches [1] and many different types of qubit system setups, such as cavity quantum electrodynamics [2], trapped ions [3, 4], nuclear magnetic resonance [5, 6] and molecular rovibrational eigenstates on electronically excited surfaces [7], have been considered.

The approach developed in our group is based on eigenstates of vibrational normal modes of polyatomic molecules encoding the qubits [8]–[13]. Recently, the idea also has been adopted for investigation by other groups [14]–[16]. Our concept of molecular quantum computation combines IR fs-spectroscopy with coherent control to design ultrafast laser pulses that act as quantum logic gates. To realize global quantum gates, a special modification of optimal control theory (OCT) [17]–[20], the multi target OCT (MTOCT) [9], is used to optimize shaped femtosecond IR laser pulses that drive the desired vibrational transitions. Earlier works on molecular quantum computation adduced the proof of principle [9, 10] for this approach and investigated the implementation of local and global gates and their induced transition mechanisms for the model system acetylene [11, 12].

With the studies presented in this paper, we systematically analyse the effects of molecular characteristics on the structure of global quantum gates and the complexity of the resulting mechanisms with the goal of rating a molecule’s suitability for molecular quantum computing. The molecules are characterized by their potential energy surface (PES) as well as by their dipole moment surfaces, which mediate the laser–molecule interaction.

Recently, a paper by Babikov [15] showed the connections between the accuracy of quantum gates and the anharmonicity of the vibrational mode encoding the qubit, based on one-dimensional (1D) model systems. We go beyond that in our investigations and in an extension to multimode systems take into account the mode coupling. The incorporation of both the anharmonicity of qubit normal modes as well as the coupling between two-qubit normal modes is realized in a parametrized 2D two-qubit model system. The parametrization is chosen such that it allows easy tuning of these characteristic properties and facilitates systematic investigations.
Moreover, the implications of the interplay of the anharmonicity and the coupling are explored.

2. Theoretical setup of qubit systems

In this study, we investigate the role of the molecular parameters anharmonicity and coupling of vibrational normal modes, that encode the qubits. To analyse the effect of anharmonic couplings, at least 2D systems have to be considered. No qualitatively new molecular interactions apart from anharmonicity and coupling would be introduced by an expansion to a higher dimensional model, therefore we confine our description to 2D systems. The nuclear kinetic Hamiltonian operator is cartesian and the considered couplings are mediated by the PESs.

To investigate the influence of anharmonicity and coupling on gate operations, several analytical 2D PES were constructed according to the power series

\[ V_{2D}(x, y) = D_x \left( 1 - \sum_{j=0}^{J} (-1)^j p^{(j)} k_x^j x^{2j} \right) + D_y \left( 1 - \sum_{l=0}^{L} (-1)^l p^{(l)} k_y^l y^{2l} \right) + \left( 1 - \sum_{m=0}^{M} q^{(m)} x^{2m} y^{2m} \right). \]

The analytic expression in equation (1) generates symmetric, anharmonic potentials and is set up in this form because we focus on asymmetric stretching vibrations of molecules, such as acetylene [11, 12] or transition metal carbonyls [13], which have been considered as qubit systems. In the power series, the coordinates \( x \) and \( y \) describe two normal modes of a molecule. The magnitude of the anharmonicity is tunable in each mode via the parameters \( p^{(j)} \) and \( p^{(l)} \), whereas \( D_x \) and \( D_y \) need to be adjusted to keep the fundamental frequencies in each case fixed. These frequencies were set constant to values of \( \omega_x = 1400 \text{ cm}^{-1} \) and \( \omega_y = 2000 \text{ cm}^{-1} \) to facilitate comparability of the various molecular settings investigated. The mode coupling is introduced by the third term and can be tuned by the parameters \( q^{(m)} \).

The parameters were varied to obtain PES with anharmonicities (defined as the difference of adjacent transitions energies \( A = E_{0\leftrightarrow 1} - E_{1\leftrightarrow 2} \) instead of \( \chi \omega \), i.e., \( A = 2\chi \omega \)) in the range of 9–45 cm\(^{-1}\) of the \( x \)-mode, which represents the lower region of typical values (\( \sim 5–180 \text{ cm}^{-1} \) [21]–[24]) of IR-chromophores. The anharmonicity range we explore is characteristic for carbonyl groups in different molecular environments. Expectedly, a high anharmonicity proves to be a favourable property for molecular qubit systems in general [15]. Thus, the control task of the systems considered in this study is more demanding. Moreover, the results can be transferred straightforwardly to PES with higher anharmonicities. The selected, constant value for the anharmonicity of the \( y \)-mode amounts to 22 cm\(^{-1}\). The coupling between the \( x \)- and \( y \)-modes is in the range 0–24 cm\(^{-1}\).

In addition an anharmonic, asymmetric PES is composed of two Morse oscillators and corresponding asymmetric and symmetric coupling terms to investigate a possible dependence of the quantum gate implementation on the PES shape

\[ V_{2D,\text{Morse}}(x, y) = D_x \left( 1 - e^{-\alpha_x x} \right)^2 + D_y \left( 1 - e^{-\alpha_y y} \right)^2 - a \cdot x y - b \cdot x^2 y - c \cdot x^2 y^2 - d \cdot x^2 y^3 - e \cdot x^3 y^2. \]
The coefficients in equation (2) were chosen, such that they fit the molecular parameters of the symmetric PES 43-8 and hence for both PES the vibrational spectra are equal (at least in the low-energy region). The notation used subsequently for the PES is composed of the anharmonicity of the second mode \(A_x\) and of the coupling \(C_{xy}\) in units of cm\(^{-1}\), \((A_x - C_{xy})\). Since the \(y\)-mode is chosen to be the passive one, its anharmonicity is not varied and it does not show up in this definition.

Selective excitation of IR-active normal modes occurs via laser–molecule interaction, mediated by the dipole moment of the molecule. The surface of the total dipole moment of the model molecule is constructed analytically as: 
\[
\mu(x, y) = a_x \cdot x + a_y \cdot y + a_0.
\]
It can be separated into two parts as two orthogonal, aslant planes, each with a slope along one vibrational normal mode. The parameters were fitted to receive transition dipole moments for both coordinates in the range of strong IR-absorbers (e.g. carbonyls), i.e. \(\mu_x = 0.45\) and \(\mu_y = 0.30\) debye. The constructed dipole surface is kept constant for all explored model PES, since the correlation between the dipole moment and the \(E\)-field is intuitively clear, i.e. a lower dipole moment would require a higher intensity for a certain excitation and vice versa.

For all PES, the corresponding vibrational eigenstates and eigenfunctions are evaluated on a grid of 256×256 points by a relaxation method, using propagation in imaginary time plus an additional diagonalization step [25]. The eigenstates are labelled in the normal mode notation \((n_y, n_x)\), which determines the level of excitation in the specific normal mode. The qubit basis is defined as previously [10]–[13]
\[
|00\rangle = |00\rangle \quad |01\rangle = |01\rangle \quad |10\rangle = |10\rangle \quad |11\rangle = |11\rangle.
\]

The transition frequencies between adjacent eigenstates within the \(x\)-normal mode, for zero and one quanta of the passive qubit in the \(y\)-mode, are presented in figure 1 for a selection of the constructed PES. We plot the transition frequencies (instead of the vibrational ladder) deliberately to facilitate a simple analysis of the calculated quantum gates and induced mechanisms. The spacing between the thick, thin and dashed black lines—and grey, respectively—reflect the anharmonicities of the systems. The influence of the coupling is mirrored in the displacement of the grey, with respect to the black lines. Increasing values of the molecular parameters result in expanded intervals, spanned by the transition frequencies.

**Figure 1.** Sequence of transition frequencies of different PES \((A_x-C_{xy})\) for the lower part of the qubit system (black) and the upper part (grey). The transition energies within the qubit basis are marked by thick lines, the first overtone excitation by a thin line and second and third by dashed lines.
3. Global quantum gates

In the following, we will describe how the relative energetical position of qubit and overtone transitions influence the characteristics of quantum gate laser fields as well as the induced mechanisms.

The quantum logic operations on a vibrational qubit basis can be induced by shaped femtosecond pulses. Appropriately shaped pulses are determined by the solution of the multi target optimal control functional [9, 10]. They are global with respect to population transfer and can be made basis set independent by a procedure presented in [12, 26]. One optimized laser field transfers the population of $k$ initial states into $k$ target states simultaneously. The initial and target states correspond to qubit basis states or linearly independent superpositions of those. All quantum gates presented were optimized for the different constructed PES with the basic requirement to reach a transfer yield above 99% for maximum intensities in the range of $10^{10}$ W cm$^{-2}$ with as short pulses as possible. These constraints should provide a basis for easier comparison of the quantum gate properties.

For an assortment of the constructed potentials a universal set of quantum gates, comprising the CNOT, NOT, Π and Hadamard gate, were calculated. All quantum gates presented in this paper operate on the second qubit (x-mode) and are global gates, as the influence of the passive qubit—in the case of the CNOT gate the control qubit—is always present and has to be coordinated by the laser pulse.

3.1. CNOT gates

A two-qubit CNOT gate performs a controlled qubit flip in the active mode, if the switching condition is fulfilled, i.e. the passive qubit is in state $|1\rangle$. This global CNOT gate induces the transitions

$$|00\rangle \rightarrow |00\rangle, \quad |01\rangle \rightarrow |01\rangle, \quad |10\rangle \rightarrow |11\rangle, \quad |11\rangle \rightarrow |10\rangle.$$  

In the Fourier (superposition) basis the effect of the CNOT gate corresponds to a conditional phase rotation (switching the phases of $|10\rangle$ and $|11\rangle$).

The CNOT quantum gate efficiencies exceed the aspired yield of 99% in compliance with the condition, that the laser pulse durations are shorter than 8000 fs, except for the systems 9-8 and 9-16. The reason for this will be explained below.

The pulse durations and maximum $E$-field intensities of the optimized CNOT pulses are specified in table 1. Both characteristic features of the optimized laser pulses are correlated, longer pulse durations in general effect lower maximum intensities. There is a general trend that an increasing anharmonicity results in shorter quantum gate laser fields. The influence of the coupling is comparatively complex and can only be explained in combination with the analysis of the switching mechanisms.

All mechanisms for the optimized CNOT gates have been calculated and two main types of CNOT switching mechanisms result, which are best represented by the systems 43-8 and 28-24. In figure 2, the optimized laser fields for two exemplary cases, the systems 43-8 and 28-24, are depicted. The upper panel shows the temporal evolution of the $E$-field, whereas the following diagram displays the cross-correlated frequency-resolved optical gating (XFROG) representation. In the lower figure, the spectral analyses of the pulses are shown, including the four key transition frequencies (two-qubit basis transition frequencies and two overtone transition
Table 1. Pulse durations and maximum intensities of different CNOT gates.

| System | 9-24 | 19-4 | 19-8 | 19-16 | 19-24 | 28-8 | 28-16 | 28-24 | 43-8 | 43-16 | 43-24 |
|--------|------|------|------|------|------|------|------|------|------|------|------|
| Pulse duration (fs) | 4354 | 7256 | 7256 | 7256 | 5805 | 2999 | 3870 | 5805 | 2999 | 2999 | 2999 |
| $I_{\text{max}}$ ($10^{10}$ W cm$^{-2}$) | 0.27 | 1.69 | 0.38 | 0.19 | 1.04 | 0.43 | 2.55 | 1.86 | 0.33 | 1.83 | 2.01 | 2.23 |

Figure 2. Optimized CNOT gates of the systems 43-8 and 28-24. The upper panels show the $E$-fields, followed by the XFROG-representations. The lower diagrams depict the spectral analyses of the CNOT pulses, including the four relevant transition frequencies for the corresponding PES. From the left- to the right-hand side the transitions are always $|11\rangle \leftrightarrow |12\rangle$, $|01\rangle \leftrightarrow |02\rangle$, $|10\rangle \leftrightarrow |11\rangle$ and $|00\rangle \leftrightarrow |01\rangle$, in the form of vertical lines. The broad frequency distribution is due to the short sub-pulses constituting the laser field and comprises also blue-shifted frequencies compared to the transition $|00\rangle \leftrightarrow |01\rangle$. The patterns of the four transition frequencies within the spectral analysis diagrams of the two presented CNOT laser fields differ as a result of the molecular parameters.

The population transfer induced by the calculated pulses in the two-qubit basis are presented for both systems in figure 3. The control mechanisms acting on the four initial states display, in case of the system 43-8, a weak intermediate excitation in the overtone states (02) and (12), shown as dashed lines. During the switching process, superposition states of initial and target qubit basis
Figure 3. Mechanisms of the action of the optimized CNOT gates on all four qubit basis states of the systems 43-8 and 28-24. The first overtone excitation is marked by the dashed line.

states are produced in all four transitions with minor oscillations of population between the qubit basis states. By the last intense sub-pulse the transitions \(|10\rangle \leftrightarrow |11\rangle\) are completed, while for \(|00\rangle\) and \(|01\rangle\) the original states are restored. The mechanisms for forward and reversed transitions \(|00\rangle \leftrightarrow |01\rangle\) and \(|10\rangle \leftrightarrow |11\rangle\) are of equal form.

The mechanism in the system 28-24, differs fundamentally from the case of 43-8. The initial state \(|00\rangle\) is barely affected by the optimized pulse, whereas most of the population of the initial qubit state \(|01\rangle\) is intermediately transferred into the overtone state \((02)\). Operating on the upper part of the qubit basis system the laser pulse performs the transitions \(|10\rangle \leftrightarrow |11\rangle\) nearly in one step eluding overtone excitation.

Now we address the question of how to explain the varying pulse durations and the obvious differences in the progression of the population transfer for the two representative systems. Both criteria are associated with the displacement of the transition frequencies (figure 2, lower panels) of the considered systems.

System 43-8 is characterized by a rather high anharmonicity of the active mode and a small potential coupling, whereas the anharmonicity of the model PES 28-24 is smaller and the coupling lies in the same range as the anharmonicity. In the case of the CNOT gate, the switching transition is given by \(|10\rangle \leftrightarrow |11\rangle\). Considering system 43-8, this frequency is detuned only 8 cm\(^{-1}\) from the transition frequency \(|00\rangle \leftrightarrow |01\rangle\). This results in an intermediate population transfer between the states not to be switched \((|00\rangle \text { and } |01\rangle)\), since both frequencies cannot be resolved by the CNOT pulse. This circumstance is also evident in the spectral analysis (figure 2, lower panel). Both transition frequencies are included in the frequency spectrum of the CNOT pulse. To evoke a qubit flip, exclusively for the states \(|10\rangle\) and \(|11\rangle\), the CNOT pulse prepares intermediate superposition states \((a_1 \cdot |00\rangle + a_2 \cdot |01\rangle) \cdot e^{i\phi_1}\) and \((b_1 \cdot |10\rangle + b_2 \cdot |11\rangle) \cdot e^{i\phi_2}\) (where \(a_i\) and \(b_i\) are complex coefficients), which are discriminated by their phase evolution alone.

In the case of system 28-24, spacing between the relevant transition frequencies of \(|00\rangle \leftrightarrow |01\rangle\) and \(|10\rangle \leftrightarrow |11\rangle\) is enlarged, compared to system 43-8, due to a higher coupling and can be discriminated by the frequency difference. For this reason the qubit basis state \(|00\rangle\) evolves unaffected of the CNOT gate operation. The higher coupling in combination with a smaller anharmonicity results in similar frequencies of the overtone excitation \(|01\rangle \leftrightarrow (02)\) and of the switching process \(|10\rangle \leftrightarrow |11\rangle\). On this account, the pulse evokes a pronounced intermediate population transfer to the state \((02)\), since both transitions cannot be distinguished.
by their frequency difference, also evident in the laser frequency spectrum (figure 2, lower panel). In this case, the superpositions \((c_1 \cdot |01⟩ + c_2 \cdot (02)) \cdot e^{i\phi_3} \) and \((b_1 \cdot |10⟩ + b_2 \cdot |11⟩) \cdot e^{i\phi_2}\) (again, \(c_i\) are complex coefficients) are discriminated again by their phase evolution.

In general, the CNOT switching mechanisms of all systems can be assigned to one of the two presented main types for the systems 43-8 and 28-24 or to a mixed variant. A similar progression and deviation of the transition frequencies evokes similar mechanisms. As in the case of system 28-24, mechanisms of the systems 19-16 and 19-24 are characterized by a significant, intermediate overtone excitation of state (02) if the CNOT gate laser pulse is acting on the qubit basis state \(|01⟩\). In all three systems the coupling is of similar size as the anharmonicity. In contrast, the molecular parameters of the systems 28-4, 28-8 and 43-16, with a higher difference in the size of coupling and anharmonicity, favour transition mechanisms that correspond to that of the system 43-8. The underlying mechanisms of the remaining systems (19-4, 19-8, 28-16 and 43-24) can be regarded as mixed types of the two main variants.

The system 9-24 is a special case. Despite the low anharmonicity of the active mode, the pulse duration is relatively short (table 1) and the mechanism is very simple. Here, the qubit basis states \(|00⟩\) and \(|01⟩\) are barely affected by the gate operation pulse, while the switching process \(|10⟩ ↔ |11⟩\) takes place. This is a result of the strong coupling as well as the large difference between the coupling and the anharmonicity leading to well-separated key transition frequencies (figure 1).

Knowledge of the quantum gate mechanisms now allows us to predict a general trend for the CNOT pulse durations (table 1) in dependence of the molecular parameters. The smaller the spacings between the characteristic transition frequencies, i.e. between \(|00⟩ ↔ |01⟩\) and \(|10⟩ ↔ |11⟩\) as well as between \(|10⟩ ↔ |11⟩\) and \(|01⟩ ↔ (02)\), the longer are the pulse durations. Especially for small couplings (e.g. systems 19-4 and 8-4) and small anharmonicities of the active mode, as well as for a coupling and anharmonicity of similar size (e.g. system 19-16) the implementation of CNOT gates requires long laser pulses or higher pulse intensities. The effects of the molecular parameters are compensated to some extent by the use of the two different mechanisms. Thus, for example, the sequence 43-8, 43-16 and 43-24 has equal pulse durations with comparable intensities. Being aware of the effects of the molecular parameters and their interplay, the difficulties of the implementation of CNOT gates shorter than 8000 fs for systems such as 9-8 and 9-16 become clear.

In conclusion, the type of mechanism and the minimum necessary pulse durations depend on the molecular parameters, which specify the spacing between the relevant transition frequencies. The interplay of the coupling and the anharmonicity determines whether the mechanism proceeds with or without overtone excitation in the state (02) starting from the qubit basis state \(|01⟩\). The pulse durations depend on the smallest transition frequency differences, that have to be resolved for the corresponding type of mechanism. A high anharmonicity always provides a broad interval for the transition frequencies and consequently is a generally favourable molecular property. Thus, in the further investigations the quantum gates are optimized for systems with anharmonicities of 28 and 43 cm\(^{-1}\) combined with three different values of the coupling 8, 16 and 24 cm\(^{-1}\).

3.2. NOT gates

A global two-qubit NOT gate induces the transitions

\(|00⟩ → |01⟩\quad |01⟩ → |00⟩\quad |10⟩ → |11⟩\quad |11⟩ → |10⟩\).

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Table 2. Pulse durations and maximum intensities of different NOT gates.

| System  | 28-8 | 28-16 | 28-24 | 43-8 | 43-16 | 43-24 |
|---------|------|-------|-------|------|-------|-------|
| Pulse duration (fs) | 4837 | 3950  | 2999  | 2477 | 2477  | 2999  |
| $I_{\text{max}}$ (10$^{10}$ W cm$^{-2}$) | 5.10 | 13.70 | 7.41  | 13.40| 8.78  | 4.58  |

Figure 4. Optimized NOT gates of the systems 43-8 and 28-24. The upper panels show the $E$-fields, followed by the XFROG-representations. The lower diagrams depict the spectral analyses of the NOT pulses, including the four relevant transition frequencies for the corresponding PES. From the left- to the right-hand side, the transitions are $|11\rangle \leftrightarrow |12\rangle$, $|01\rangle \leftrightarrow |02\rangle$, $|10\rangle \leftrightarrow |11\rangle$ and $|00\rangle \leftrightarrow |01\rangle$.

In contrast to the CNOT gate, the qubit flips occur irrespective of the state of the first qubit and for this reason the transition frequencies $|00\rangle \leftrightarrow |01\rangle$ and $|10\rangle \leftrightarrow |11\rangle$ do not need to be resolved by the NOT pulse.

The duration and intensities of the optimized NOT laser fields are presented in table 2. Again, two different representative mechanisms can be identified and are best reflected in the systems 43-8 and 28-24. The corresponding laser fields and their XFROG representations, as well as the spectral analyses with the characteristic transition frequencies marked are shown in figure 4.

The NOT gate pulse of the system 43-8 turns out to be 522 fs shorter than that for the system 28-24, both providing gate efficiencies above 99%. The maximum pulse intensities are higher compared to those of the corresponding CNOT gates and the pulses’ frequency range is generally broader, as both transitions in the qubit basis have to be driven now by the laser
Figure 5. Mechanisms of the action of the optimized NOT gates on all four qubit basis states of the systems 43-8 and 28-24. The first overtone excitation is marked by the dashed line and the second by the dotted line.

field. The mechanisms induced in both model systems are displayed in figure 5. The underlying mechanism for the model system 43-8 is characterized by a single-step switching process after 1300 fs of the total pulse duration with preliminary oscillation between the initial and target qubit basis states and a slight, intermediate overtone excitation. In contrast, the overtone (02) of system 28-24 is populated significantly throughout most of the pulse duration, starting from either |00⟩ or |01⟩. For the upper part of the qubit system, however, population transfer out of the qubit basis into the state |12⟩ can nearly be suppressed.

Both mechanisms as well as the differing pulse durations can be understood referring to the spectral analyses (figure 4, lower panels). Due to the small coupling in the system 43-8, the qubit basis states |00⟩ and |10⟩—as well as |01⟩ and |11⟩—are affected by the pulse in the same way, i.e. in this case, the population transfer mechanisms do not depend on the state of the passive qubit. Furthermore, the overtone states play a minor role as a result of the high anharmonicity and their spectral intensity is vanishing. The NOT switching mechanisms of the systems 28-8 and 43-16 exhibit a similar progression of the population transfer as shown for the system 43-8, due to a similar relation of coupling and anharmonicity. The NOT gate pulse durations increase in this series with decreasing deviation of the two molecular parameters and with a decreasing coupling.

For the model system 28-24 both molecular parameters are of similar size and consequently the transition frequencies |10⟩ ↔ |11⟩ and |01⟩ ↔ (02) are not resolved by the laser pulse. Thus, the state (02) is intermediately strongly populated. This is also the case for the systems 43-24 and 28-16. For this mechanism type, the difference between the characteristic transition frequencies plays no role in the pulse durations. The dominant factor is now the total range of the interval, spanned by the relevant transition frequencies (compare figure 1 and table 2). Proportional to this range the pulse durations and/or the intensities decrease.

3.3. Significance of anharmonicity and coupling for qubit flip gates

The role of the anharmonicity for the realization of quantum gates is clear. The anharmonicity helps to distinguish the relevant transitions for the implementation of quantum logic gates from
unwanted overtone excitations and thus makes the system controllable by laser interaction. In compliance with [15], we found that a higher anharmonicity is in general a favourable property in order to receive efficient and non-complex quantum gate laser fields. Here, we specifically focus on the role of the vibrational mode coupling.

To emphasize its importance for the implementation of CNOT gates, we investigated switching gates (CNOT and NOT) in a non-coupled 2D system (43-0). Correspondingly to our previous examinations of weakly coupled systems, a CNOT gate cannot be implemented for anharmonic, non-coupled systems, since neither the transition frequencies nor the phase evolution can be resolved. On the other hand, the implementation of a NOT gate in such a system turns out to be straightforward and facile, since both switching transitions require the same frequency. The corresponding simply structured and short (1200 fs) NOT gate consists of only two sub-pulses with the same carrier frequency of 1400 cm$^{-1}$. The mechanism of the NOT gate is a smooth, adiabatic and single-step switching process.

The coupling between the qubit normal modes, which is necessary for the implementation of conditional gates (e.g. CNOT gates), reflects the entanglement in the qubit system. In the qubit basis, it results in different transition frequencies for $|n0\rangle \leftrightarrow |n1\rangle$ with $n$ equals 0 or 1. The coupling, i.e. the entanglement, is always present and is utilized or suppressed during the action of a quantum gate laser pulse. For example, a CNOT gate is achieved either by resolving the transition frequency difference or via the different phase evolution of the intermediate superposition states.

3.4. $\Pi$ Gates

In $\Pi$ gates, the phases of quantum states are addressed during the gate operation. If the second qubit state is initially in $|1\rangle$ the $\Pi$ gate evokes a phase shift of $\pi$.

Since the MTOCT functional is not sensitive to global phase shifts of the wavefunction, the $\Pi$ gate needs to be optimized operating on superposition states of pure basis states [8]

$$\frac{1}{\sqrt{2}}(|00\rangle + |01\rangle) \leftrightarrow \frac{1}{\sqrt{2}}(|00\rangle - |01\rangle),$$

$$\frac{1}{\sqrt{2}}(|10\rangle + |11\rangle) \leftrightarrow \frac{1}{\sqrt{2}}(|10\rangle - |11\rangle).$$

In general, all optimized $\Pi$ gates turn out to be shorter than the previous qubit flip gates, as can be seen in table 3. The maximum laser field intensities are similar to intensities of the corresponding NOT gates. The general trend of pulse durations with respect to the anharmonicity is again traceable. Systems with higher anharmonicities require shorter pulses and as for the NOT gate in combination with an increasing coupling the maximum pulse intensities decrease.
Figure 6. Optimized $\Pi$ gates of the systems 43-8 and 28-24. The upper panels show the $E$-fields, followed by the XFROG-representations. The lower diagrams depict the spectral analyses of the $\Pi$ pulses, including the four relevant transition frequencies for the corresponding PES. From the left- to the right-hand side, the transitions are $|11\rangle \leftrightarrow (|12\rangle$, $|01\rangle \leftrightarrow (|02\rangle$, $|10\rangle \leftrightarrow |11\rangle$ and $|00\rangle \leftrightarrow |01\rangle$.

Again, we present two optimized laser fields (figure 6) and mechanisms (figure 7) for the model systems 43-8 and 28-24. The qubit basis states participating in the 50:50 superposition state interchange population during several oscillations and finally the initial composition of the superposition state is restored. Longer pulses and consequently a higher frequency resolution is expected to decrease the number of oscillations.

For the mechanism of system 43-8 (as well as 28-8 and 43-16), the intermediate overtone population is low compared to that of the model systems 28-24 (figure 7), 28-16 and 43-24. This is reflected in the spectral analyses (figure 6, lower panels) of both optimized $\Pi$ gates. Similar to the NOT gate, the $\Pi$ gate laser pulse of system 43-8 includes only the two-qubit basis transition frequencies in its spectrum. In contrast, the $\Pi$ pulse of system 28-24 cannot resolve the close lying transition frequencies $|10\rangle \leftrightarrow |11\rangle$ and $|01\rangle \leftrightarrow (02\rangle$. Consequently, the overtone (02) is strongly populated intermediately, if the $\Pi$ gate laser pulse is operating on the superposition basis state $|00\rangle - |01\rangle$. The superposition state $|00\rangle + |01\rangle$ differs only in the phase relation between the qubit basis states and due to interference effects the intermediate overtone excitation is weaker. Again, the spectral width, comprising the relevant transition frequencies, is decisive for the durations and maximum intensities of the optimized $\Pi$ quantum gate laser fields.
Figure 7. Mechanisms of the action of the optimized Π gates of the systems 43-8 and 28-24, starting from the superposition states (a) $\frac{1}{\sqrt{2}}(|00\rangle + |01\rangle) \rightarrow \frac{1}{\sqrt{2}}(|00\rangle - |01\rangle)$, (b) $\frac{1}{\sqrt{2}}(|00\rangle - |01\rangle) \rightarrow \frac{1}{\sqrt{2}}(|00\rangle + |01\rangle)$, (c) $\frac{1}{\sqrt{2}}(|10\rangle + |11\rangle) \rightarrow \frac{1}{\sqrt{2}}(|10\rangle - |11\rangle)$ and (d) $\frac{1}{\sqrt{2}}(|10\rangle - |11\rangle) \rightarrow \frac{1}{\sqrt{2}}(|10\rangle + |11\rangle)$. The first overtone excitation is marked by the dashed line and the second by the dotted line.

Table 4. Pulse durations and maximum intensities of different Hadamard gates.

| System        | 28-8 | 28-16 | 28-24 | 43-8 | 43-16 | 43-24 |
|---------------|------|-------|-------|------|-------|-------|
| Pulse duration (fs) | 7257 | 5806  | 5806  | 4838 | 3870  | 3300  |
| $I_{\max}$ ($10^{10}$ W cm$^{-2}$) | 3.98 | 13.80 | 2.66  | 5.64 | 4.03  | 2.38  |

3.5. Hadamard gates

The gate which completes the universal set of quantum gates is the Hadamard operation and we optimized it for the same systems as the NOT and Π gate. The optimized transitions are, as for the Π gate, based on superposition states

$$\frac{1}{\sqrt{2}}(|00\rangle + |10\rangle) \leftrightarrow \frac{1}{2}(|00\rangle + |01\rangle + |10\rangle + |11\rangle),$$

$$\frac{1}{\sqrt{2}}(|01\rangle + |11\rangle) \leftrightarrow \frac{1}{2}(|00\rangle - |01\rangle + |10\rangle - |11\rangle).$$

Babikov states better implementation prospects for Hadamard transformations in comparison with NOT operations in his 1D investigations of local gates [15]. In our expanded systematic investigations of coupled 2D systems, we optimize the Hadamard gate globally and even basis set independently (including the forward and backward transformations). Accordingly, the optimization task for the global Hadamard gate is more demanding than for the previous logical gates. Correct control of population transfer and additionally control of the phase evolution of the wavepacket is required. Consequently, the calculated Hadamard gates acquire more complex structures, longer pulse durations (table 4) as well as more complicated mechanisms.
Figure 8. Optimized Hadamard gate of the system 43-8. The upper panel on the left-hand side shows the \( E \)-field, followed by the XFROG-representation. The lower diagram depicts the spectral analysis of the Hadamard pulse, including the four relevant transition frequencies. From the left- to the right-hand side the transitions are \(|11\rangle \leftrightarrow (|2\rangle, |0\rangle \leftrightarrow (|2\rangle, |1\rangle \leftrightarrow |11\rangle \) and \(|0\rangle \leftrightarrow |01\rangle \). On the right-hand side the forward and backward mechanisms, with the transitions (a) \(|0\rangle \leftrightarrow \frac{1}{\sqrt{2}}(|00\rangle + |01\rangle)\), (b) \(|01\rangle \leftrightarrow \frac{1}{\sqrt{2}}(|00\rangle - |01\rangle)\), (c) \(|10\rangle \leftrightarrow \frac{1}{\sqrt{2}}(|10\rangle + |11\rangle)\) and (d) \(|11\rangle \leftrightarrow \frac{1}{\sqrt{2}}(|10\rangle - |11\rangle)\), are depicted. The first overtone excitation is marked by the dashed line and the second by the dotted line.

In general, the maximum intensities (table 4) of the \( E \)-fields are in between the intensities of the NOT and \( \Pi \) gates. As can be derived from this table, increasing anharmonicities and couplings of the systems tend to yield shorter Hadamard gate laser pulses.

We present the optimized laser field (\( E \)-field, XFROG-representation and spectral analysis on the left-hand side of figure 8) and the forward and backward mechanisms (on the right-hand side) for one selected system 43-8. In contrast to the previous gates for this system, the frequencies of the overtone transitions \(|01\rangle \leftrightarrow (|2\rangle \) and \(|11\rangle \leftrightarrow (|2\rangle \) are both included in the spectrum of the Hadamard gate pulse (figure 8, spectral representation) and as a consequence the population is intermediate stored to a great extent in the overtone states, as displayed in the mechanism in figure 8. Moreover, the population transfer is highly oscillatory. The Hadamard pulse drives all desired transitions by discriminating the phase evolution of superposition states. For the maximum pulse duration used (8000 fs), we find only this single type of mechanism. The degree of overtone excitation depends on the deviation of the anharmonicity and the coupling and it is expected to decrease with longer pulse durations.
Table 5. Residual population (%) of vibrational states after the action of optimized CNOT gates with different total durations $T$ on the qubit basis state $|01\rangle$, in this case the initial and target state. The target state population is marked bold.

| $T$   | $|00\rangle$ | $|01\rangle$ | $|02\rangle$ |
|------|--------------|--------------|--------------|
| 1239 fs | 20.87        | **77.31**    | 0.02         |
| 1439 fs | 16.57        | **81.31**    | 0.05         |
| 1858 fs | 11.99        | **85.92**    | 1.70         |
| 2477 fs | 6.08         | **93.61**    | 0.01         |
| 2999 fs | 0.02         | **99.59**    | 0.01         |
| 5338 fs | ~0           | **99.96**    | ~0           |

3.6. Implementation of quantum gates in an asymmetric, anharmonic PES

The previously presented optimized quantum gates operate on 2D model systems with a symmetric, anharmonic PES. Additionally, we constructed an asymmetric, 2D Morse potential, which features the same molecular parameters as the system 43-8 and apply the universal set of quantum gates optimized for the symmetric anharmonic system 43-8. We find that the quantum gates operate with the same efficiencies and according to the same mechanisms as for the symmetric system. The deviations are marginal and only show up in case of overtone excitations e.g. in the mechanism of the Hadamard gate. Consequently, we can exclude a dependence of the quantum gate implementation on the symmetry of the PES with respect to the equilibrium geometry.

The transferability of the optimized gates leads us to the conclusion that the anharmonicity and coupling, defining the molecular properties, are crucial for the structure of the quantum gates and the induced mechanisms, for a selected qubit basis. Hence, the suitability of molecules for molecular quantum computation can be judged by considering these parameters.

3.7. ‘Optimal’ quantum gate implementation

The quantum gate laser fields shown above were optimized with efficiencies above 99%. The choice of preferably short laser pulses leads to the identification of a necessary minimum pulse duration which ensures the required frequency resolution. This circumstance can be verified by means of table 5, which lists the residual population in relevant qubit states after the operation of optimized CNOT gates on the state $|01\rangle$ with different pulse durations $T$ for the model system 43-8.

In our preceding analysis, we linked the features of the resulting laser fields and the mechanisms induced to the pattern of the relevant transition frequencies. All previously presented pulses of minimum duration contain to a large extent blue-shifted frequencies, with respect to the ground state transition frequency. The broad frequency spectrum originates from the short sub-pulses. It covers the qubit basis transitions and preferably excludes frequencies further red-shifted, since overtone excitation has to be suppressed as far as possible. As a result higher, superfluous frequencies occur on the blue side band and yield complex laser fields.

Consequently, it should be possible to increase the gate duration such that simply structured laser fields and simple mechanisms are obtained. Not all systems are equally suitable to realize
Figure 9. Optimized CNOT, NOT and Hadamard gate of the system 43-8. The upper panels show the $E$-field and the lower diagrams depict the spectral analysis of both quantum gate pulses, including the four relevant transition frequencies. From the left- to the right-hand side the transitions are $|11\rangle \leftrightarrow |12\rangle$, $|01\rangle \leftrightarrow |02\rangle$, $|10\rangle \leftrightarrow |11\rangle$ and $|00\rangle \leftrightarrow |01\rangle$.

this step in practice, since some of the gate durations were already quite long. For a proof of principle, we selected the model system 43-8 to search for the ‘optimal’ duration for the CNOT, NOT and Hadamard gates. They are displayed together with their spectral analysis, in figure 9.

As a result of the increased duration the laser field structures become very simple with sequences of two to three sub-pulses. In case of the CNOT gate, the laser field spectrum includes mainly the frequency of the switching process and to a minor part the transition frequency $|00\rangle \leftrightarrow |01\rangle$. Evidently, it is not necessary to totally suppress this transition frequency in order to obtain experimentally feasible laser pulses and simple mechanisms. The frequency distribution of the NOT and Hadamard pulse comprise only the two required transition frequencies $|10\rangle \leftrightarrow |11\rangle$ and $|00\rangle \leftrightarrow |01\rangle$. Now, with these extended pulse durations, the frequency resolution is sufficient to separate the required from the non-relevant transition frequencies. The corresponding mechanisms turn out to be smooth and simple, eluding overtone excitation.

Accordingly it may be expected, that an extension of the pulse duration helps to enable the implementation of all quantum gates, even for systems with unfavourable molecular properties, such as 9-8.

4. Conclusion

In the present work, we investigated systematically the effect of molecular properties on the feasibility of quantum gates. Therefore, we optimized a universal set of quantum gates for several model potentials, with varying anharmonicities and potential couplings. Furthermore, the effort was to keep the quantum gate laser pulses as short as possible with a limited intensity, while reaching a fidelity of virtually 100%. We showed, that the structural simplicity of the pulses and of the mechanisms increases with ascending pulse durations. Thus, the complexity of the
optimized quantum gate laser fields depends on the gate length. For converged runs with equal
gate lengths one receives very similar or even identical laser fields.

Our calculations demonstrate that in general it is possible to implement highly efficient
elementary global quantum gates, i.e. CNOT, NOT, Π and Hadamard gate, for all symmetric or
asymmetric, anharmonic and coupled 2D systems. The optimization of a series of CNOT gates
reveals the importance of the potential coupling. In a non-coupled system, the implementation of
a CNOT gate is not possible and weak couplings, in the range of a few wavenumbers, in general
tend to yield long CNOT gates with complex mechanisms. Nevertheless, systems exhibiting
small couplings can provide rather short and simple CNOT gates (43-8) if the anharmonicity
exceeds the coupling by far. Thus, we conclude that the interplay of anharmonicity and coupling
plays the decisive role for the CNOT gates and determines whether overtone excitation can be
suppressed or not. The NOT gate performs unconditional switching operations and therefore a
small coupling, combined with a high anharmonicity are favourable molecular features.

The Π gate requires the control of the relative phase of the qubit basis states, which is
achieved via intermediate population transfer. Again a certain frequency resolution is required
and the associated degree of complexity shows in the varying pulse duration. Overall, Π gates
turn out to be distinctly shorter than the qubit flip gates. The global Hadamard gate is the most
complex gate since it requires phase and population control. According to this, the minimum
pulse durations exceed the previous gates. As for the NOT gates, the complexity of the Π and
Hadamard gate laser fields and the degree of overtone excitation is correlated with the ratio of
anharmonicity and coupling.

In general, the separation of the qubit basis from the overtone transition frequencies in the
vibrational ladder is important for all essential quantum gates and thus a high anharmonicity
is favourable. The degree of the coupling gives rise to two different effects. The coupling is
essential for the implementation of the CNOT gate, whereas it complicates the optimization of
NOT gates—as well as Π and Hadamard gates. In conclusion, promising molecular parameters
are characterized by a moderate coupling and a high anharmonicity and thus by a preferably high
difference between both parameters. We performed this study based on systems exhibiting rather
low anharmonicities, which generally demand a higher control task. The results can be easily
transferred to systems with higher anharmonicities. For instance, OH-stretching vibrations with
anharmonicities (in our definition) of $A \sim 180 \text{ cm}^{-1}$ represent in this sense more adequate qubit
systems [15]. In general this will yield shorter pulse durations.

We identified the anharmonicity and the coupling as crucial properties and rated their
effect on the complexity of quantum gates. No new aspects are expected to emerge for higher-
dimensional molecular qubit systems, since only the relative transition frequency differences,
that are governed by these parameters, define the controllability and control mechanisms.

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