Experiment 8. Electronic structure calculations on diatomic molecules

The postulates and theorems of quantum mechanics form the rigorous foundation for the prediction of chemical properties from first principles. Fundamental postulates of quantum mechanics – microscopic systems are described by 'wave functions' that completely characterize all of the physical properties of the system. Quantum mechanical 'operators' correspond to each physical observable that, when applied to the wave function, allow one to predict the probability of finding the system to exhibit a particular value or range of values for that observable.

In particular, quantum mechanical calculations are able to compute the structure of a molecule. The calculations are usually carried out for isolated molecules – the fundamental unit from which pure substances are constructed. The minimum information to specify a molecule is its molecular formula (the atoms of which it is composed) and the manner in which those atoms are connected. What is required is simply to know the relative positions of all atoms in space. The 'best' structure – has the lowest possible energy given an overall connectivity roughly dictated by the starting positions of the atoms as chosen by the theoretician. Geometry optimization in terms of energy minimization will give us then the best (optimal) structure.

The fundamental postulate of quantum mechanics – wave function exists for any chemical system, appropriate operators (functions) which act upon Ψ return the observable properties of the system:

$$\vartheta\Psi = e\Psi$$

ϑ is an operator, e is a scalar value for some property of the system. When the equation holds, Ψ is an eigenfunction, e is an eigenvalue. The probability that a chemical system will be found within some region of multidimensional space is equal to the integral of $|\Psi|^2$ over that region of space. The postulates place certain constraints on an acceptable wave function: 1) for a bound particle, the normalized integral of $|\Psi|^2$ over all space must be unity (the probability of finding it somewhere is one); 2) Ψ must be continuous and single-valued.

The operator that returns the system energy, E, as an eigernvalue is called Hamiltonian operator:

$$H\Psi = E\Psi$$ - **Shrödinger equation**

The Hamiltonian operator takes into account five contributions to the total energy: the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions:

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_e}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

$\hbar$ is Plank's constant divided by 2π; ∇^2 is the Laplasian operator:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

The Hamiltonian operator is composed from the kinetic and potential energy parts. The potential energy parts are the same as in classical mechanics. The kinetic energy for a QM particle is not $|\mathbf{p}|^2/2m$ but $T = -\frac{\hbar^2}{2m}\nabla^2$.

The Born-Oppenheimer Approximation

Under typical conditions, the nuclei of molecular systems are moving much more slowly than the electrons (proton and neutrons are ~1800 times more massive than electrons) and electronic relaxation with respect to nuclear motion is instantaneous. It is convenient to decouple these two motions and compute electronic energies for fixed nuclear positions. The nuclear kinetic motion term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. The electronic Schrödinger equation:

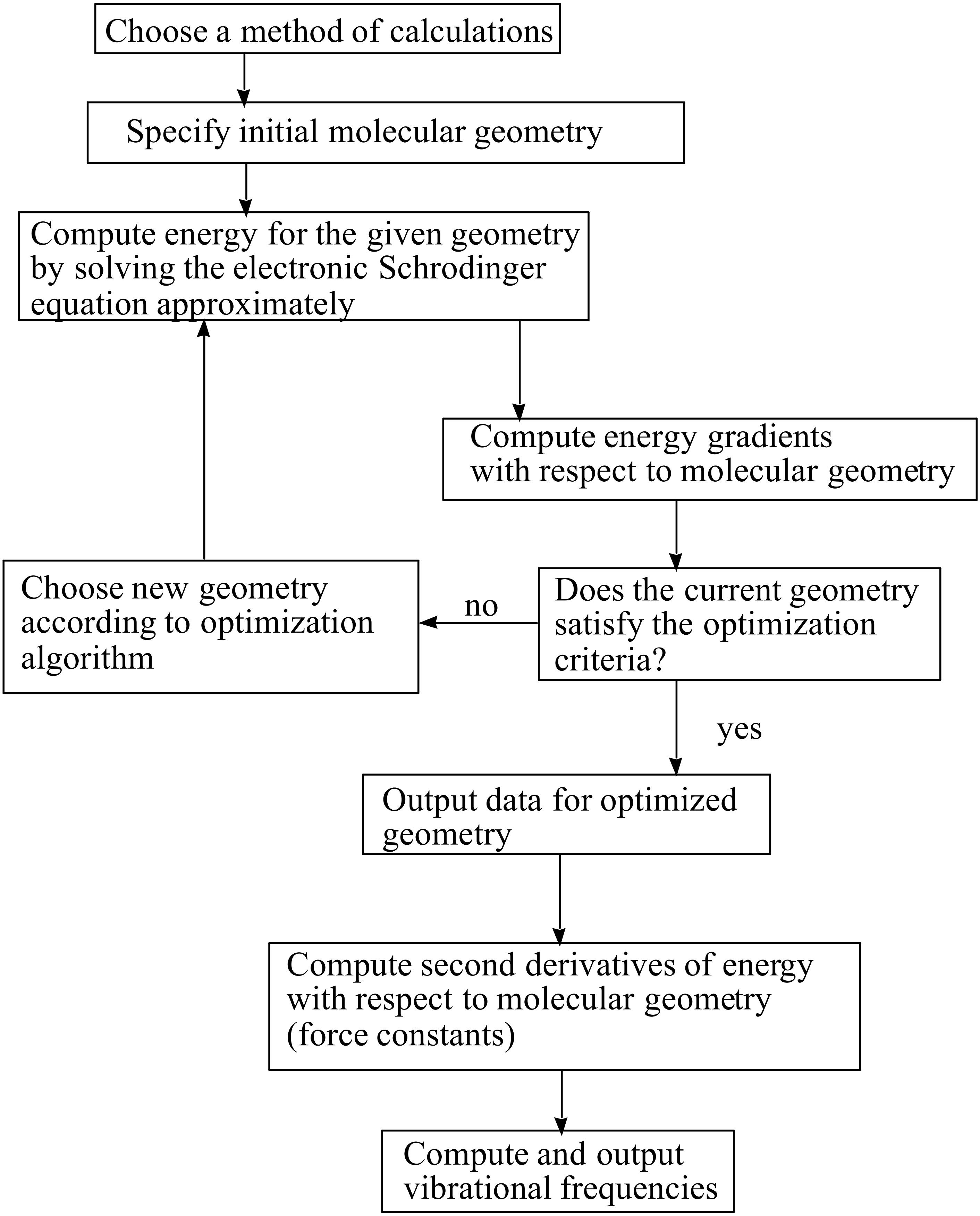
$$(H_{el} + V_N)\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k) = E_{\mathrm{el}}\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k)$$

Wave functions are invariant to the appearance of constant term in the Hamiltonian – in practice, one can almost always solve this equation without the inclusion of V_N and then add V_N to the obtained eigenvalue to obtain E_{el}.

The Born-Oppenheimer approximation is entirely justified in most cases. It has very profound consequences and allows us to use the concept of a potential energy surface (PES): The PES is the surface defined by E_{el} over all possible nuclear coordinates. This means that we can determine electronic energy for a certain set of nuclear coordinates by solving the electronic Schrödinger equation. Then, by minimizing the energy with respect to nuclear coordinates - using gradients of the energy (first derivatives of the energy with respect to interatomic distances, bond angles and torsional angles) - we can find the equilibrium structure of a molecule. Finally, through calculations of second derivatives of the energy with respect to nuclear coordinates (force constants), we can compute vibrational frequencies, which can be observed experimentally using IR and Raman spectroscopy.

The electronic Schrödinger equation cannot be solved exactly for many-electron systems. However, various approximate methods exist to obtain a solution to a certain level of accuracy. These methods are mathematically complex (they are presented in the graduate course CHM5586, *Computational Chemistry*) and cannot be applied without the use of powerful computers. Fortunately, in recent decades sophisticated computer programs have been developed for this purpose, which allow a 'non-expert' to perform quantum chemical calculations. The most popular among these programs are HyperChem and GAUSSIAN. In this experiment, students will use the Windows version of the GAUSSIAN program to compute geometric structure and vibrational frequencies for diatomic molecules. This task requires from the user to prepare a GAUSSIAN input file containing a starting molecular geometry and specifying the method for calculations (for solving the electronic Schrödinger equation) and their type (geometry optimization, calculation of vibrational frequencies, etc.). After that, the program is submitted and the calculations will determine the optimal geometry (the structure that has a minimal energy on the potential energy surface) and vibrational frequency for the molecule of interest.

The general scheme how the GAUSSIAN program performs quantum chemical calculations is illustrated on the following flow-chart: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Compute energy for the given geometry by solving the electronic Schrodinger equation approximately
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Does the current geometry satisfy the optimization criteria?
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Choose new geometry according to optimization algorithm
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Output data for optimized geometry
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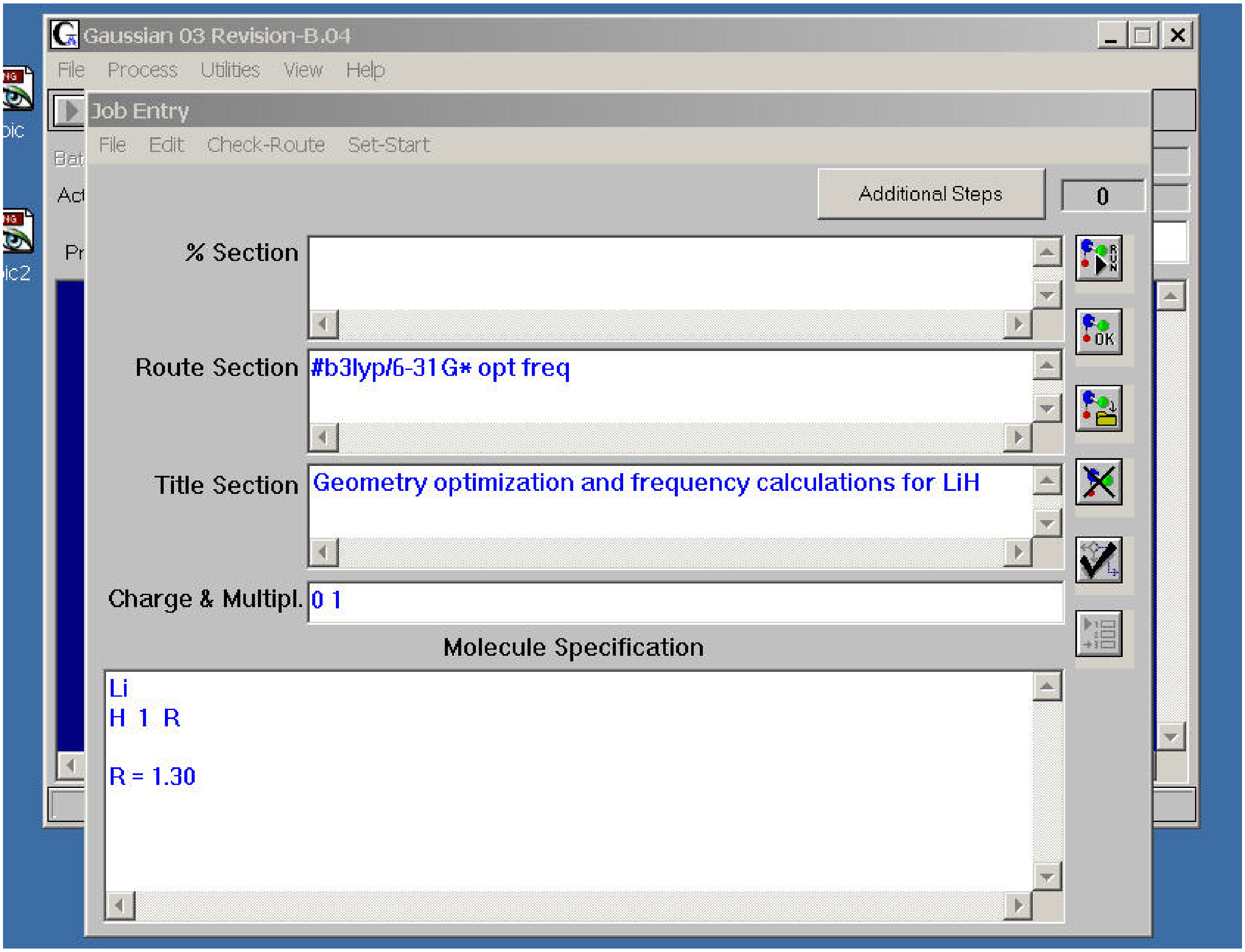
‘Experimental’

Chose a diatomic molecule for calculations. It is recommended that it was the molecule for which the student carried out literature search in the PChem Lab I CHM3410L course. Submit GAUSSIAN program on the PC in the PChem Lab and type in the input data that include the method of calculations, molecular charge and multiplicity, and initial molecular geometry:



Route Section #b3lyp/6-31G* opt freq

Title Section Geometry optimization and frequency calculations for LiH

Charge & Multipl. 0 1

```
Li
H 1 R

R = 1.30
```

Route section specifies the method and the type of calculations. The method is a quantum chemical procedure to be used to find an approximate solution for the electronic Schrödinger equation and the basis set for molecular wave function. The calculations should be carried out employing three different methods:

1) The Hartree-Fock method ‘HF’: this is the simplest ‘ab initio’ (from the first principles) method, in which the molecular many-electron wave function is expressed as a determinant composed from one-electron wave functions of all electrons in the molecule. The HF method is time-efficient but rather approximate, since it does not take into account the correlation between motion of different electrons in the molecule (electronic correlation): each electron is assumed to be moving in an average field created by all other electrons (and by nuclei).

2) The Møller-Plesset second-order perturbation theory method (MP2): this is the cheapest and most efficient method, which takes into account electronic correlation to some extent. It should be more accurate than HF.

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The basis set is specified after the ‘/’. The need to have a basis set in the GAUSSIAN calculations is related to the fact that the wave function for each electron in the molecule is expressed as a linear combination of atomic orbitals, i.e. the orbitals of the hydrogen-atom type. The basis set specifies how many hydrogen-atom type s, p, d, etc., orbitals are included. In these calculations, students will use the 6-31G* basis set.

In summary, in this experiment three following calculations will be performed:

1. # hf/6-31g*
2. # mp2/6-31g*
3. # b3lyp/6-31g*

The type of calculations is also specified in the route section with keywords ‘opt’ and ‘freq’. The ‘opt’ keyword means ‘optimization’; the program is requested to optimize molecular geometry, i.e., to find the structure with the lowest potential energy. The ‘freq’ keyword specifies calculations of vibrational frequencies. These two keywords should be present in all three calculations.

The **title section** includes an arbitrary comment describing your calculations. It will be also found in the output file.

The **charge and multiplicity** section indicates molecular charge and multiplicity. For the neutral molecules, the charge is specified as ‘0’. The multiplicity is the number of unpaired electrons in the molecule + 1, i.e., ‘1’ for singlet, ‘2’ for doublet, ‘3’ for triplet, etc.

The **molecular specification** section is used to input initial molecular geometry. It is specified in the form of atomic Cartesian coordinates or a so-called z-matrix, which shows interatomic distances, bond angles, and torsional angles. In the case of a diatomic molecule, students need to specify only the two atoms comprising the molecule and the distance between them:

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Li
H   1   R
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Here, the first atom in the molecule is lithium ‘Li’ and the second is hydrogen ‘H’ and the Li-H distance is designated with the variable ‘R’, which will be optimized during the calculations. The initial values for this variable is given (in angstrom) after a blank line:

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After the input is prepared, click the ‘Run’ button to submit calculations. You will then be prompted to specify a name for the output file and the calculations will run.

As the calculations are completed, open the output file with a word processor (MsWord). The output file contains a lot of information including molecular potential energy calculated for each optimization step, wave function expressed as linear combination of atomic orbitals in the basis set, orbital energies, atomic electric charges, etc. The required information is the optimized interatomic distance and the vibrational frequency, which are given as follows:

```
-- Stationary point found.
                          ----------------------------
                          !   Optimized Parameters   !
                          ! (Angstroms and Degrees)  !
 -----------------------                      ------------------------
 ! Name  Definition            Value         Derivative Info.          !
 --------------------------------------------------------------------------
 ! R1    R(1,2)               1.6209        -DE/DX =    0.             !
 --------------------------------------------------------------------------
```

and

```
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                  1
                 SG
 Frequencies --  1399.1094
 Red. masses --     1.1293
 Frc consts  --     1.3024
 IR Inten    --   117.6770
 Raman Activ --     0.0000
 Depolar     --     0.0000
 Atom AN      X      Y      Z
   1   3     0.00   0.00   0.14
   2   1     0.00   0.00  -0.99
```

For LiH, these results show that the optimal Li-H bond length is 1.6209 Å and the vibrational frequency is 1399 cm^{-1}.

The lab report should include the results (interatomic distances and vibrational frequencies) of the calculations using three different methods, HF/6-31g*, MP2/6-31g*, and B3LYP/6-31g*. In the discussion, compare your calculated results with the literature data (experimental and theoretical) and compare the accuracy of different methods versus experimental values. Also sketch the molecular orbital energy diagram for your molecule, deduce its ground state electronic configuration, and multiplicity. Compare the deduced electronic configuration with the calculated one – the GAUSSIAN output provides calculated energies of the occupied and vacant molecular orbitals.

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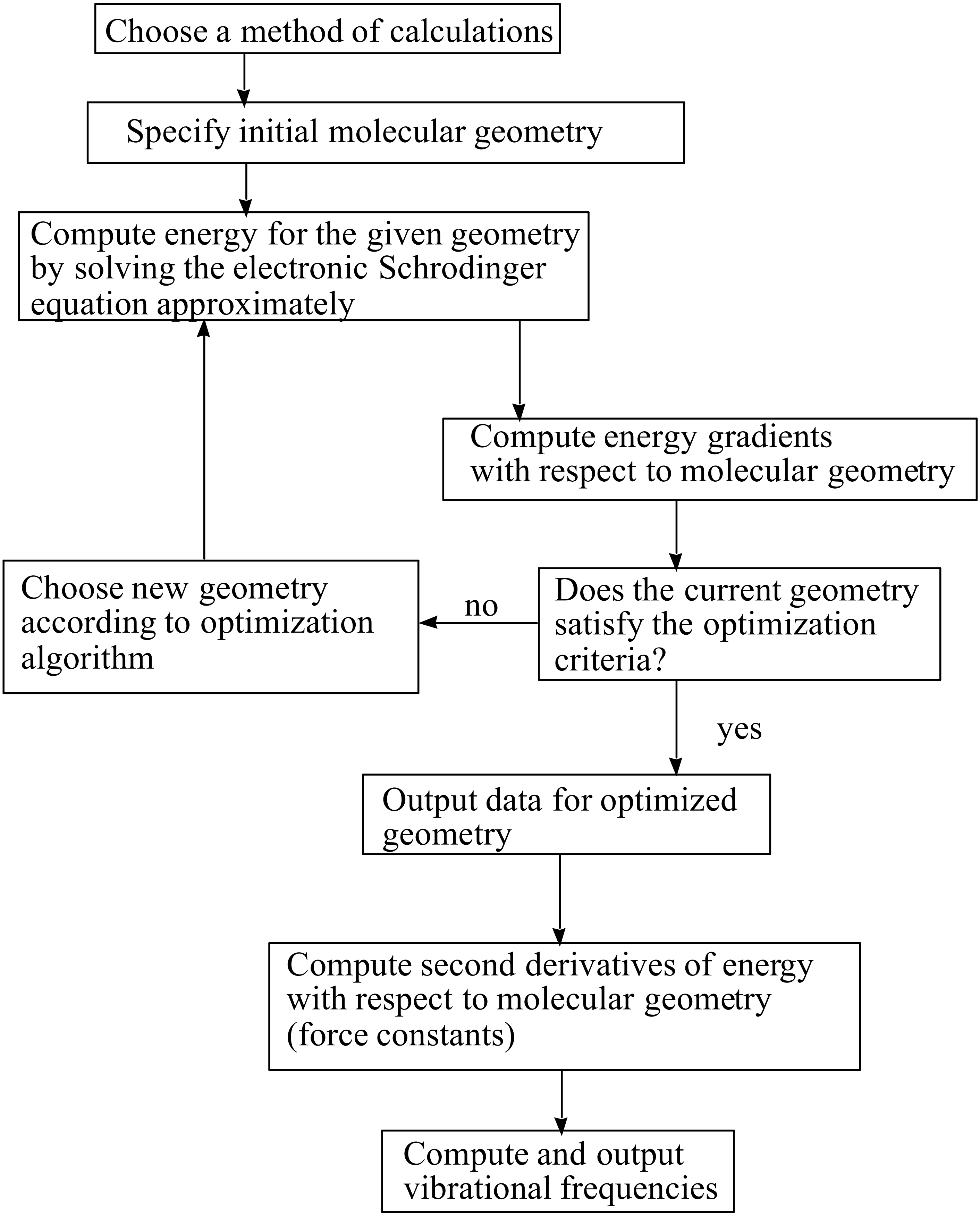
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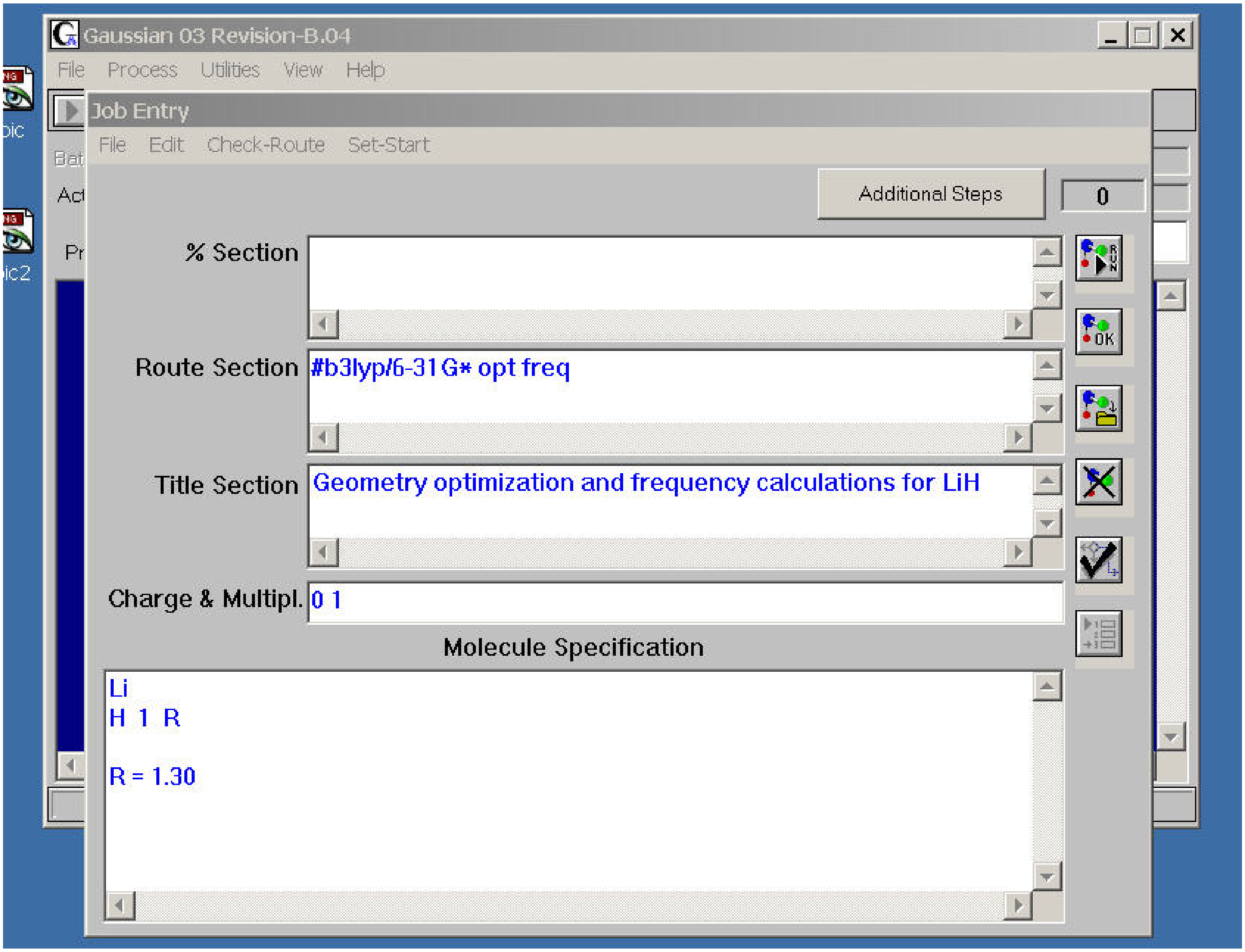

% Section

Route Section #b3lyp/6-31G* opt freq

Title Section Geometry optimization and frequency calculations for LiH

Charge & Multipl. 0 1

Molecule Specification

```
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```
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                          ----------------------------
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 ---------------------------------------------------------------------------
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 ---------------------------------------------------------------------------
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 Frequencies --  1399.1094
 Red. masses --     1.1293
 Frc consts  --     1.3024
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 Depolar     --     0.0000
 Atom AN      X      Y      Z
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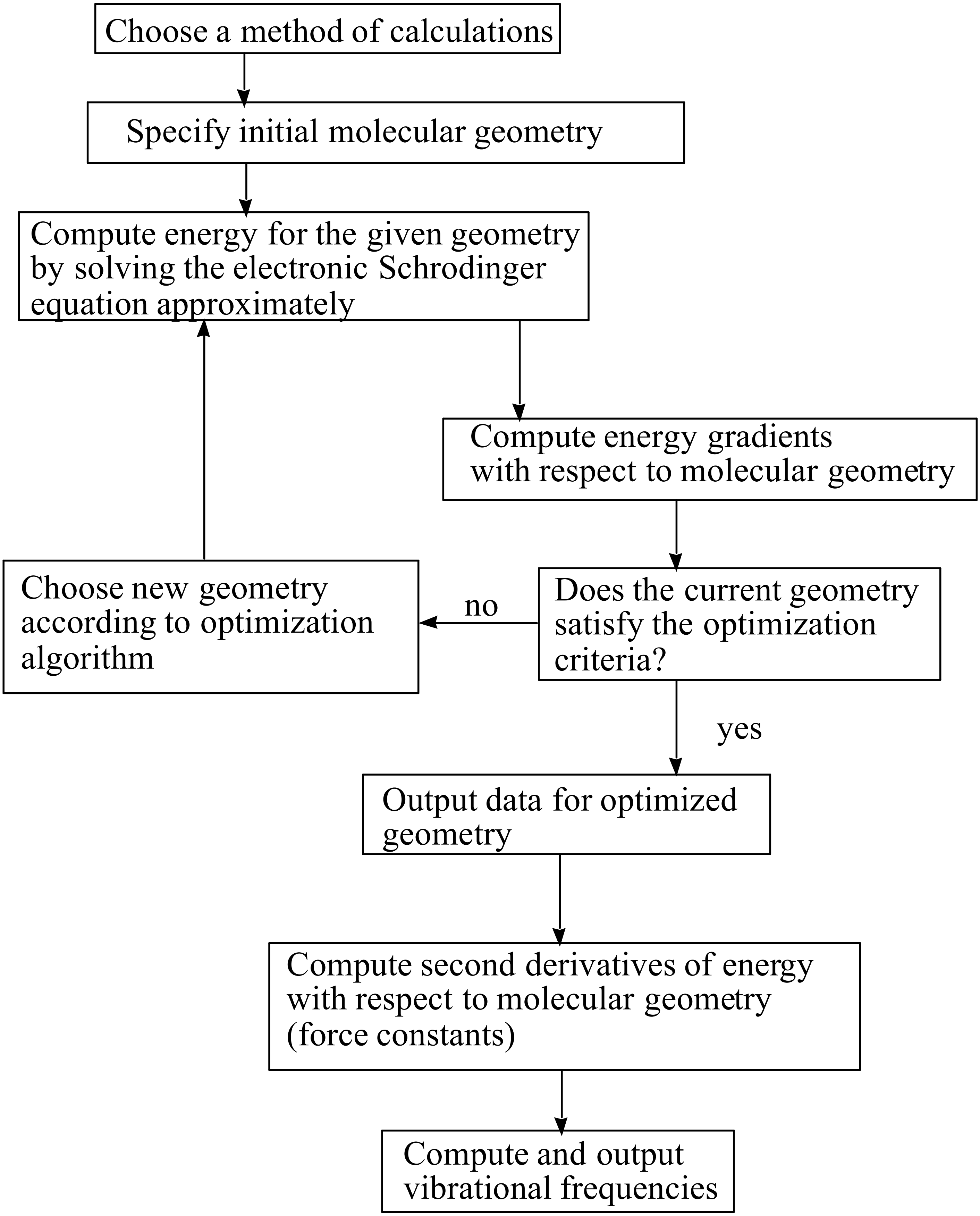
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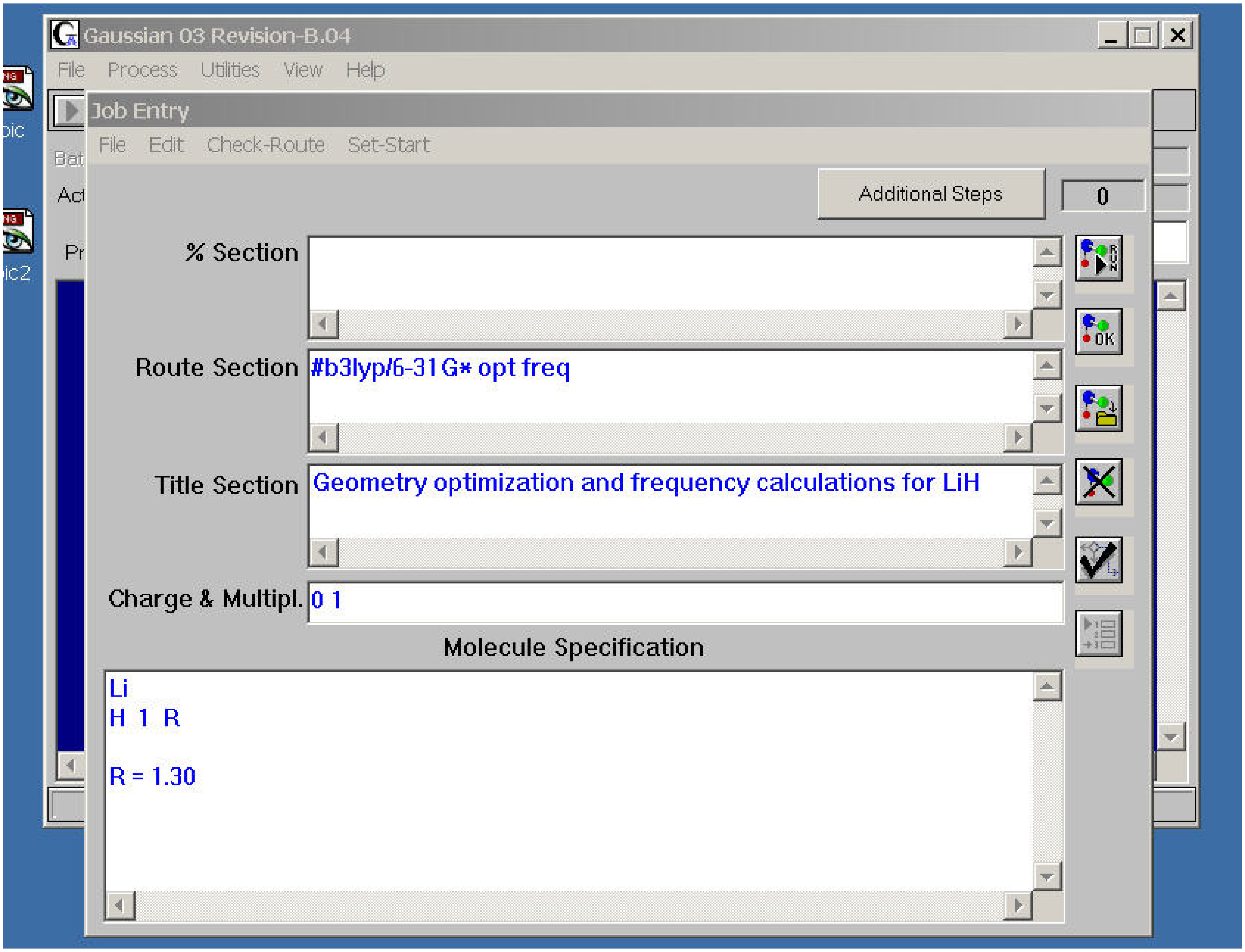

Route Section: #b3lyp/6-31G* opt freq

Title Section: Geometry optimization and frequency calculations for LiH

Charge & Multipl.: 0 1

```
Li
H  1  R

R = 1.30
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```
-- Stationary point found.
                        ----------------------------
                        !   Optimized Parameters   !
                        ! (Angstroms and Degrees)  !
 -----------------------                  ------------------------
 ! Name  Definition           Value        Derivative Info.          !
 ---------------------------------------------------------------------
 ! R1    R(1,2)               1.6209      -DE/DX =    0.            !
 ---------------------------------------------------------------------
```

and

```
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                  SG
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Experiment 8. Electronic structure calculations on diatomic molecules

The postulates and theorems of quantum mechanics form the rigorous foundation for the prediction of chemical properties from first principles. Fundamental postulates of quantum mechanics – microscopic systems are described by ‘wave functions’ that completely characterize all of the physical properties of the system. Quantum mechanical ‘operators’ correspond to each physical observable that, when applied to the wave function, allow one to predict the probability of finding the system to exhibit a particular value or range of values for that observable.

In particular, quantum mechanical calculations are able to compute the structure of a molecule. The calculations are usually carried out for isolated molecules – the fundamental unit from which pure substances are constructed. The minimum information to specify a molecule is its molecular formula (the atoms of which it is composed) and the manner in which those atoms are connected. What is required is simply to know the relative positions of all atoms in space. The ‘best’ structure – has the lowest possible energy given an overall connectivity roughly dictated by the starting positions of the atoms as chosen by the theoretician. Geometry optimization in terms of energy minimization will give us then the best (optimal) structure.

The fundamental postulate of quantum mechanics – wave function exists for any chemical system, appropriate operators (functions) which act upon Ψ return the observable properties of the system:

$$\vartheta\Psi = e\Psi$$

ϑ is an operator, e is a scalar value for some property of the system. When the equation holds, Ψ is an eigenfunction, e is an eigenvalue. The probability that a chemical system will be found within some region of multidimensional space is equal to the integral of $|\Psi|^2$ over that region of space. The postulates place certain constraints on an acceptable wave function: 1) for a bound particle, the normalized integral of $|\Psi|^2$ over all space must be unity (the probability of finding it somewhere is one); 2) Ψ must be continuous and single-valued.

The operator that returns the system energy, E, as an eigernvalue is called Hamiltonian operator:

$$H\Psi = E\Psi \qquad - \qquad \textbf{Shrödinger equation}$$

The Hamiltonian operator takes into account five contributions to the total energy: the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions:

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_e}\nabla_k^2 - \sum_i\sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{k<l}\frac{e^2 Z_k Z_l}{r_{kl}}$$

$\hbar$ is Plank's constant divided by 2π; ∇^2 is the Laplasian operator:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

The Hamiltonian operator is composed from the kinetic and potential energy parts. The potential energy parts are the same as in classical mechanics. The kinetic energy for a QM particle is not $|\mathbf{p}|^2/2m$ but $T = -\frac{\hbar^2}{2m}\nabla^2$.

The Born-Oppenheimer Approximation

Under typical conditions, the nuclei of molecular systems are moving much more slowly than the electrons (proton and neutrons are ~1800 times more massive than electrons) and electronic relaxation with respect to nuclear motion is instantaneous. It is convenient to decouple these two motions and compute electronic energies for fixed nuclear positions. The nuclear kinetic motion term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. The electronic Schrödinger equation:

$$(H_{el} + V_N)\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k) = E_{\mathrm{el}}\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k)$$

Wave functions are invariant to the appearance of constant term in the Hamiltonian – in practice, one can almost always solve this equation without the inclusion of V_N and then add V_N to the obtained eigenvalue to obtain E_{el}.

The Born-Oppenheimer approximation is entirely justified in most cases. It has very profound consequences and allows us to use the concept of a potential energy surface (PES): The PES is the surface defined by E_{el} over all possible nuclear coordinates. This means that we can determine electronic energy for a certain set of nuclear coordinates by solving the electronic Schrödinger equation. Then, by minimizing the energy with respect to nuclear coordinates - using gradients of the energy (first derivatives of the energy with respect to interatomic distances, bond angles and torsional angles) - we can find the equilibrium structure of a molecule. Finally, through calculations of second derivatives of the energy with respect to nuclear coordinates (force constants), we can compute vibrational frequencies, which can be observed experimentally using IR and Raman spectroscopy.

The electronic Schrödinger equation cannot be solved exactly for many-electron systems. However, various approximate methods exist to obtain a solution to a certain level of accuracy. These methods are mathematically complex (they are presented in the graduate course CHM5586, *Computational Chemistry*) and cannot be applied without the use of powerful computers. Fortunately, in recent decades sophisticated computer programs have been developed for this purpose, which allow a 'non-expert' to perform quantum chemical calculations. The most popular among these programs are HyperChem and GAUSSIAN. In this experiment, students will use the Windows version of the GAUSSIAN program to compute geometric structure and vibrational frequencies for diatomic molecules. This task requires from the user to prepare a GAUSSIAN input file containing a starting molecular geometry and specifying the method for calculations (for solving the electronic Schrödinger equation) and their type (geometry optimization, calculation of vibrational frequencies, etc.). After that, the program is submitted and the calculations will determine the optimal geometry (the structure that has a minimal energy on the potential energy surface) and vibrational frequency for the molecule of interest.

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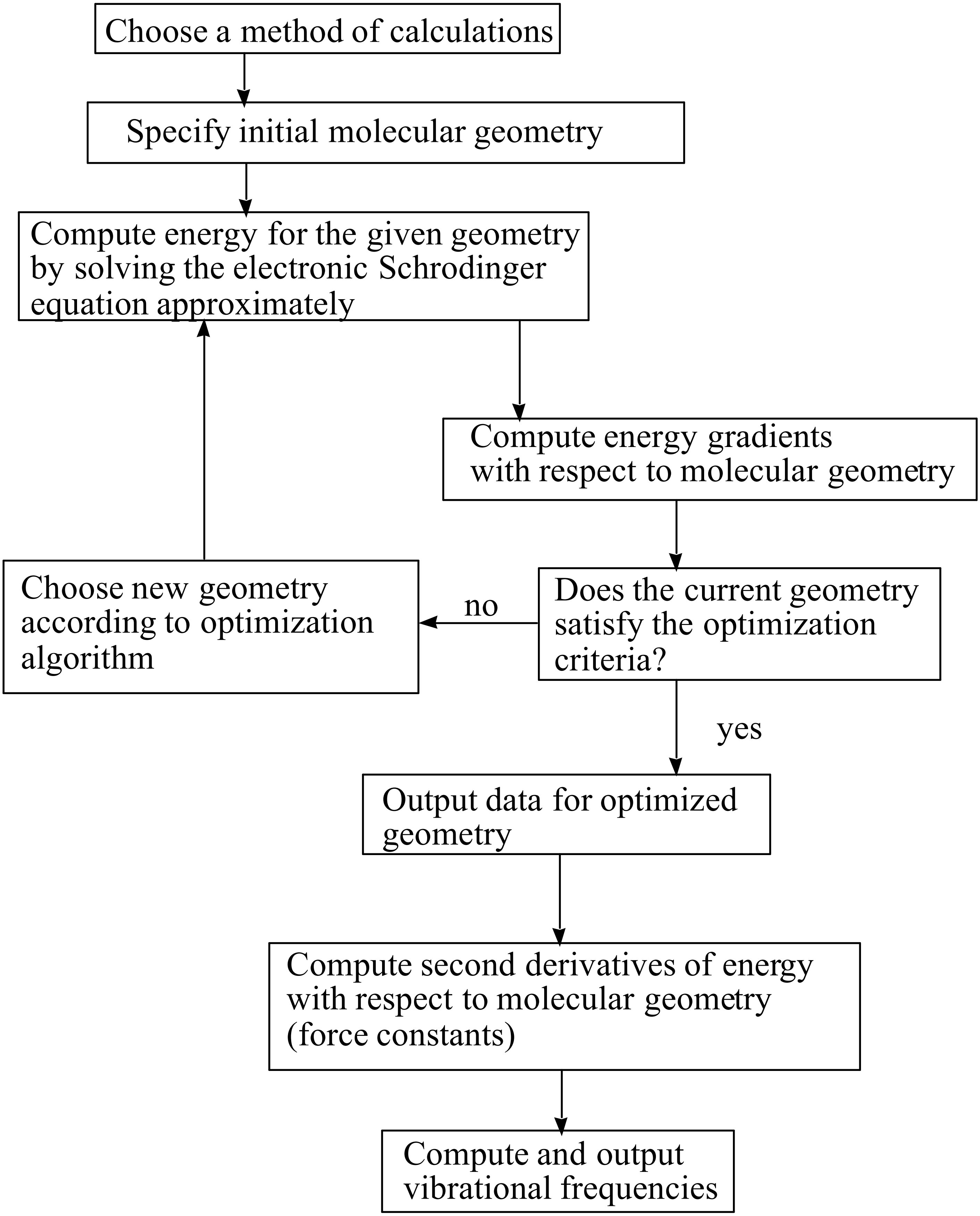
Choose a method of calculations
Specify initial molecular geometry
Compute energy for the given geometry by solving the electronic Schrodinger equation approximately
Compute energy gradients with respect to molecular geometry
Does the current geometry satisfy the optimization criteria?
no
Choose new geometry according to optimization algorithm
yes
Output data for optimized geometry
Compute second derivatives of energy with respect to molecular geometry (force constants)
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‘Experimental’

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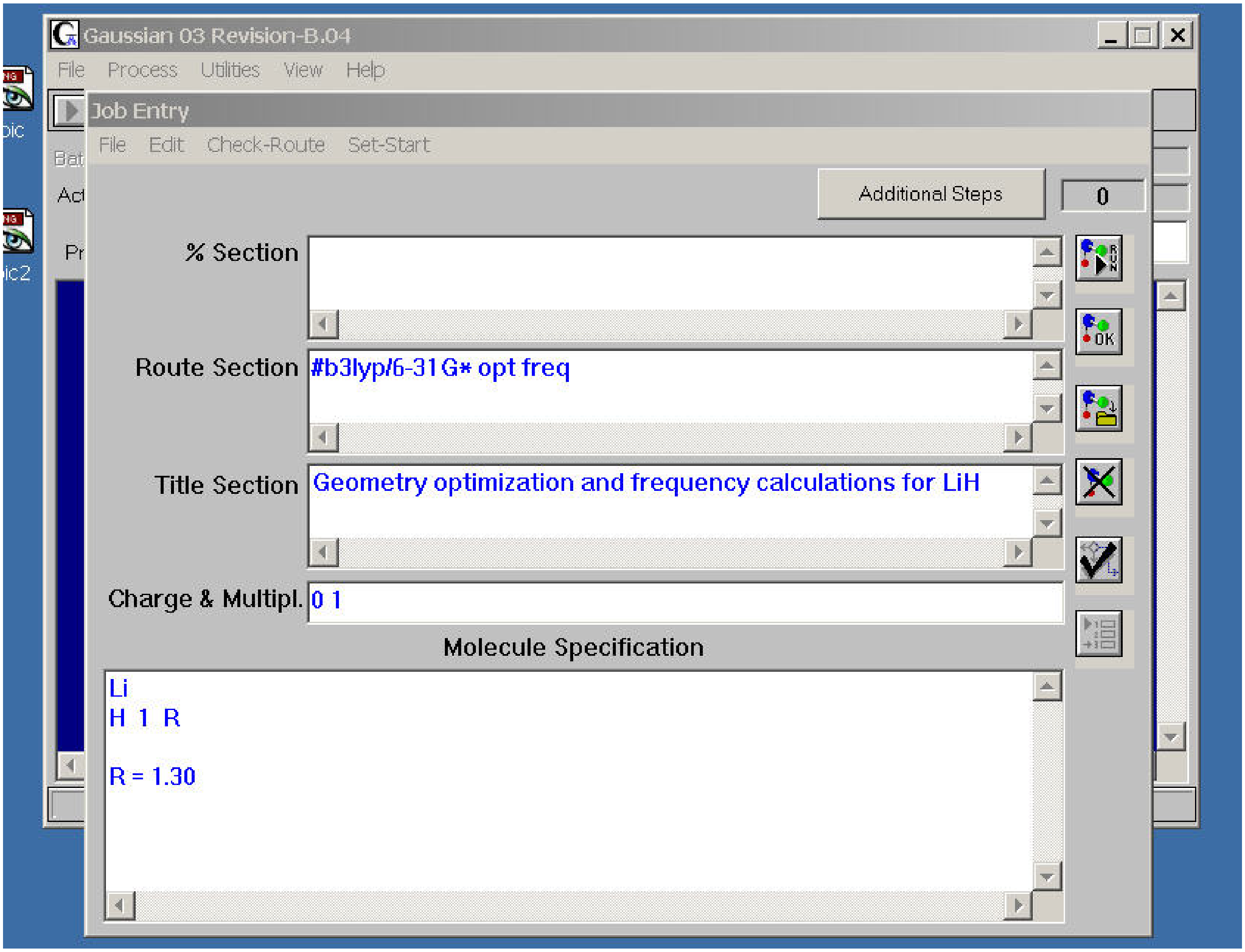

% Section:

Route Section: #b3lyp/6-31G* opt freq

Title Section: Geometry optimization and frequency calculations for LiH

Charge & Multipl.: 0 1

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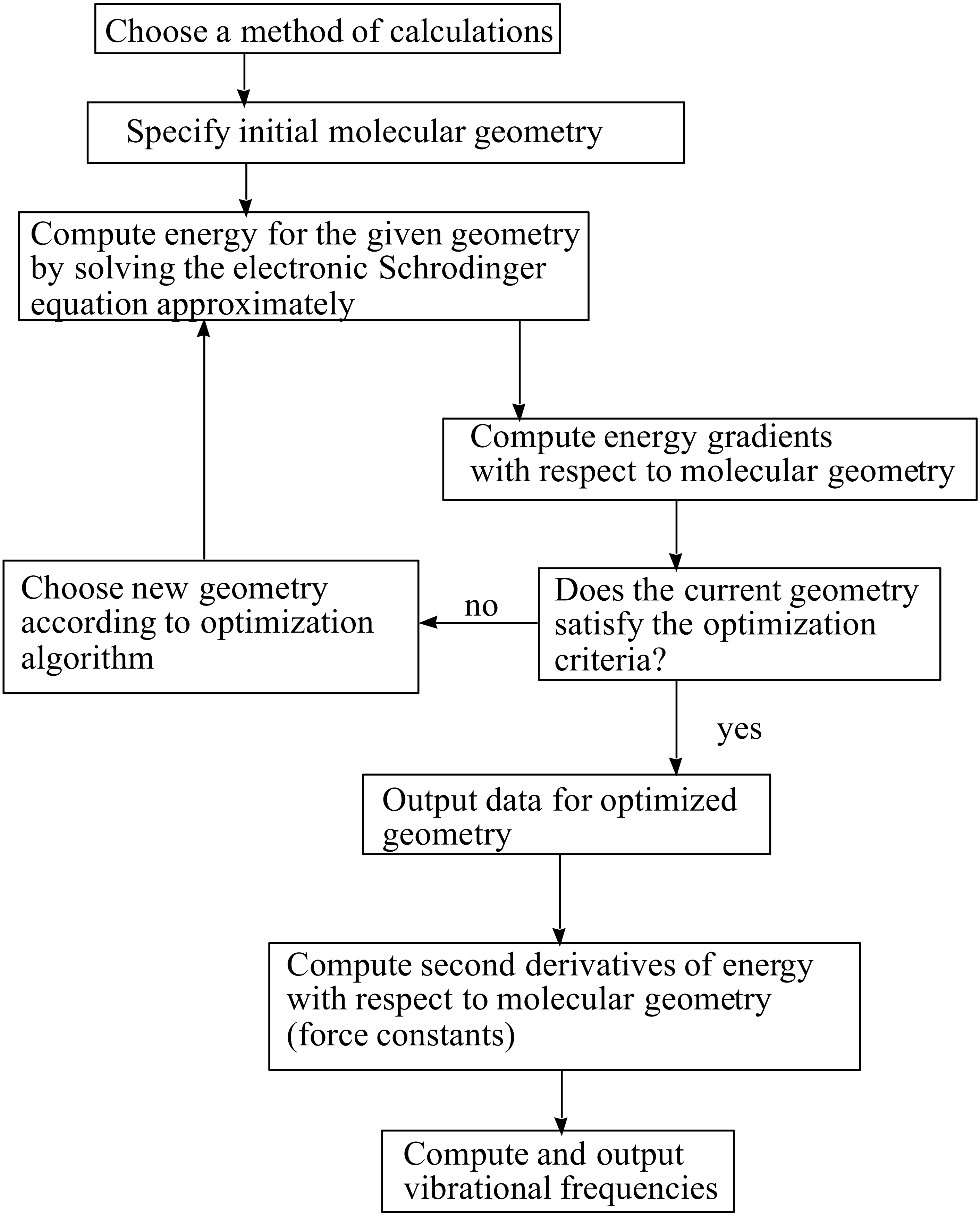
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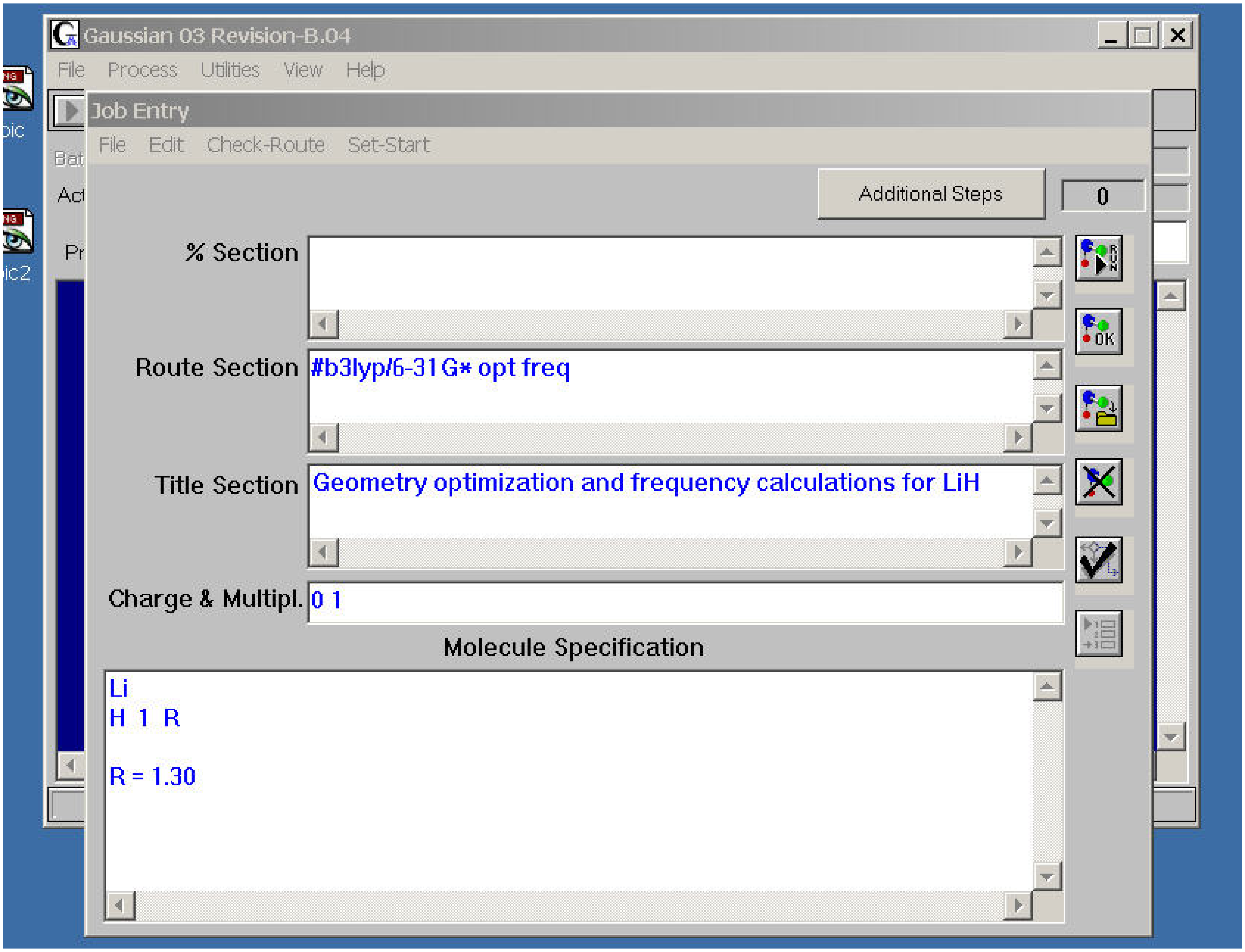

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In particular, quantum mechanical calculations are able to compute the structure of a molecule. The calculations are usually carried out for isolated molecules – the fundamental unit from which pure substances are constructed. The minimum information to specify a molecule is its molecular formula (the atoms of which it is composed) and the manner in which those atoms are connected. What is required is simply to know the relative positions of all atoms in space. The 'best' structure – has the lowest possible energy given an overall connectivity roughly dictated by the starting positions of the atoms as chosen by the theoretician. Geometry optimization in terms of energy minimization will give us then the best (optimal) structure.

The fundamental postulate of quantum mechanics – wave function exists for any chemical system, appropriate operators (functions) which act upon Ψ return the observable properties of the system:

$$\vartheta\Psi = e\Psi$$

ϑ is an operator, e is a scalar value for some property of the system. When the equation holds, Ψ is an eigenfunction, e is an eigenvalue. The probability that a chemical system will be found within some region of multidimensional space is equal to the integral of $|\Psi|^2$ over that region of space. The postulates place certain constraints on an acceptable wave function: 1) for a bound particle, the normalized integral of $|\Psi|^2$ over all space must be unity (the probability of finding it somewhere is one); 2) Ψ must be continuous and single-valued.

The operator that returns the system energy, E, as an eigernvalue is called Hamiltonian operator:

$$H\Psi = E\Psi$$ - **Shrödinger equation**

The Hamiltonian operator takes into account five contributions to the total energy: the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions:

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_e}\nabla_k^2 - \sum_i\sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{k<l}\frac{e^2 Z_k Z_l}{r_{kl}}$$

$\hbar$ is Plank's constant divided by 2π; ∇^2 is the Laplasian operator:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

The Hamiltonian operator is composed from the kinetic and potential energy parts. The potential energy parts are the same as in classical mechanics. The kinetic energy for a QM particle is not $|\mathbf{p}|^2/2m$ but $T = -\frac{\hbar^2}{2m}\nabla^2$.

The Born-Oppenheimer Approximation

Under typical conditions, the nuclei of molecular systems are moving much more slowly than the electrons (proton and neutrons are ~1800 times more massive than electrons) and electronic relaxation with respect to nuclear motion is instantaneous. It is convenient to decouple these two motions and compute electronic energies for fixed nuclear positions. The nuclear kinetic motion term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. The electronic Schrödinger equation:

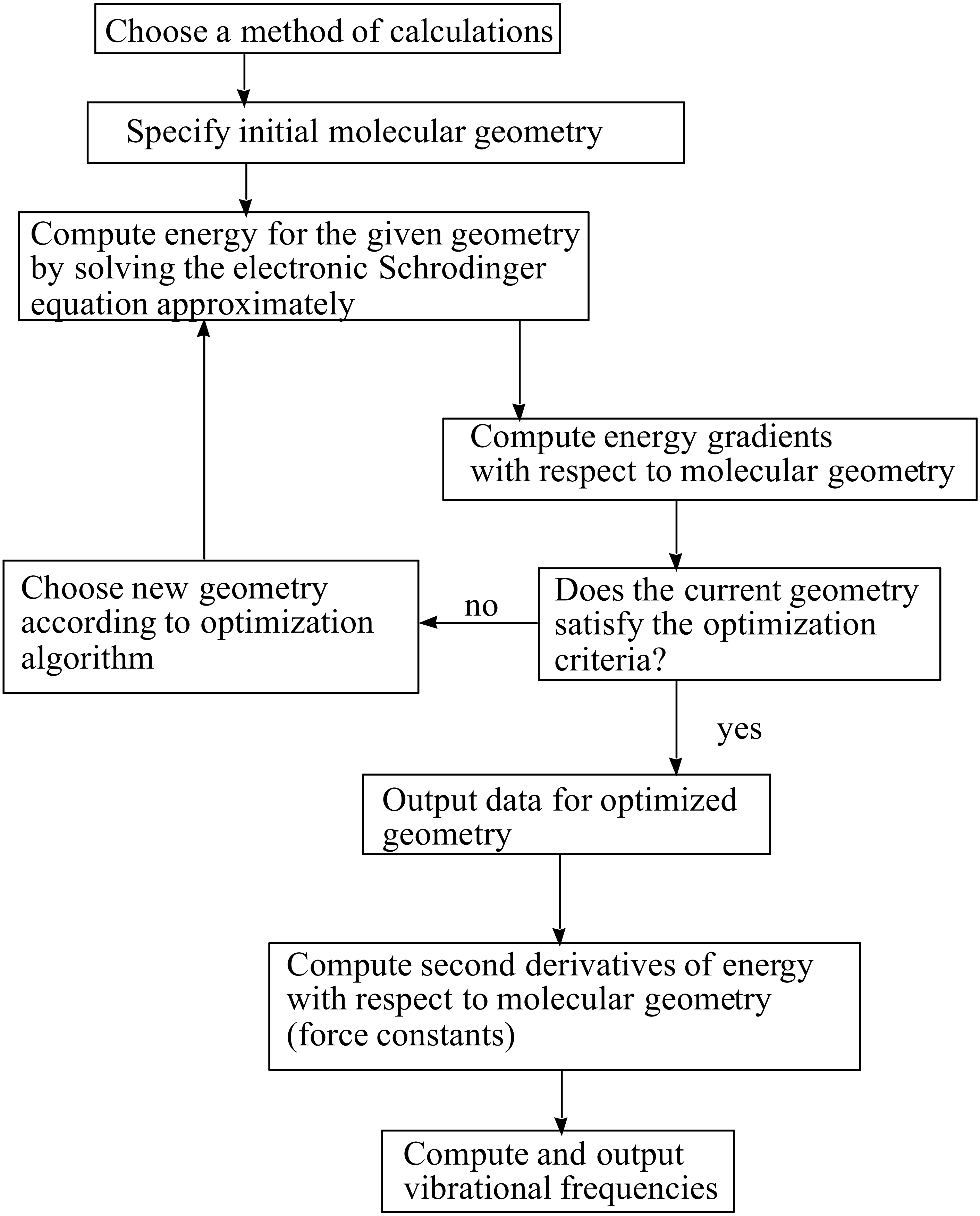
$$(H_{el} + V_N)\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k) = E_{\mathrm{el}}\Psi_{\mathrm{el}}(\mathbf{q}_i;\mathbf{q}_k)$$

Wave functions are invariant to the appearance of constant term in the Hamiltonian – in practice, one can almost always solve this equation without the inclusion of V_N and then add V_N to the obtained eigenvalue to obtain E_{el}.

The Born-Oppenheimer approximation is entirely justified in most cases. It has very profound consequences and allows us to use the concept of a potential energy surface (PES): The PES is the surface defined by E_{el} over all possible nuclear coordinates. This means that we can determine electronic energy for a certain set of nuclear coordinates by solving the electronic Schrödinger equation. Then, by minimizing the energy with respect to nuclear coordinates - using gradients of the energy (first derivatives of the energy with respect to interatomic distances, bond angles and torsional angles) - we can find the equilibrium structure of a molecule. Finally, through calculations of second derivatives of the energy with respect to nuclear coordinates (force constants), we can compute vibrational frequencies, which can be observed experimentally using IR and Raman spectroscopy.

The electronic Schrödinger equation cannot be solved exactly for many-electron systems. However, various approximate methods exist to obtain a solution to a certain level of accuracy. These methods are mathematically complex (they are presented in the graduate course CHM5586, *Computational Chemistry*) and cannot be applied without the use of powerful computers. Fortunately, in recent decades sophisticated computer programs have been developed for this purpose, which allow a 'non-expert' to perform quantum chemical calculations. The most popular among these programs are HyperChem and GAUSSIAN. In this experiment, students will use the Windows version of the GAUSSIAN program to compute geometric structure and vibrational frequencies for diatomic molecules. This task requires from the user to prepare a GAUSSIAN input file containing a starting molecular geometry and specifying the method for calculations (for solving the electronic Schrödinger equation) and their type (geometry optimization, calculation of vibrational frequencies, etc.). After that, the program is submitted and the calculations will determine the optimal geometry (the structure that has a minimal energy on the potential energy surface) and vibrational frequency for the molecule of interest.

The general scheme how the GAUSSIAN program performs quantum chemical calculations is illustrated on the following flow-chart: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Compute energy gradients with respect to molecular geometry
Does the current geometry satisfy the optimization criteria?
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Choose new geometry according to optimization algorithm
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Output data for optimized geometry
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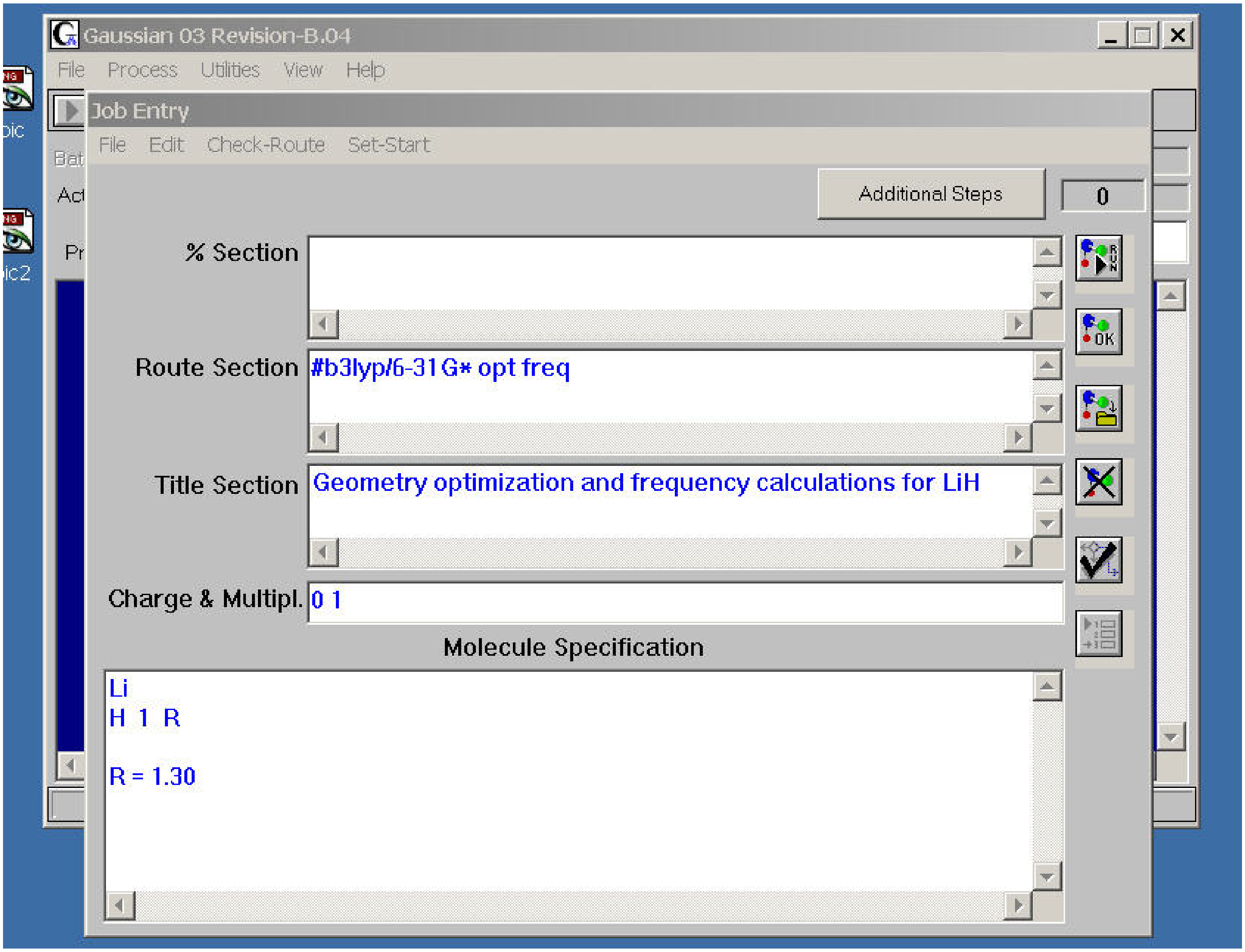
‘Experimental’

Chose a diatomic molecule for calculations. It is recommended that it was the molecule for which the student carried out literature search in the PChem Lab I CHM3410L course. Submit GAUSSIAN program on the PC in the PChem Lab and type in the input data that include the method of calculations, molecular charge and multiplicity, and initial molecular geometry:



% Section

Route Section: #b3lyp/6-31G* opt freq

Title Section: Geometry optimization and frequency calculations for LiH

Charge & Multipl.: 0 1

```
Li
H 1 R

R = 1.30
```

Route section specifies the method and the type of calculations. The method is a quantum chemical procedure to be used to find an approximate solution for the electronic Schrödinger equation and the basis set for molecular wave function. The calculations should be carried out employing three different methods:

1) The Hartree-Fock method ‘HF’: this is the simplest ‘ab initio’ (from the first principles) method, in which the molecular many-electron wave function is expressed as a determinant composed from one-electron wave functions of all electrons in the molecule. The HF method is time-efficient but rather approximate, since it does not take into account the correlation between motion of different electrons in the molecule (electronic correlation): each electron is assumed to be moving in an average field created by all other electrons (and by nuclei).

2) The Møller-Plesset second-order perturbation theory method (MP2): this is the cheapest and most efficient method, which takes into account electronic correlation to some extent. It should be more accurate than HF.

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The basis set is specified after the ‘/’. The need to have a basis set in the GAUSSIAN calculations is related to the fact that the wave function for each electron in the molecule is expressed as a linear combination of atomic orbitals, i.e. the orbitals of the hydrogen-atom type. The basis set specifies how many hydrogen-atom type s, p, d, etc., orbitals are included. In these calculations, students will use the 6-31G* basis set.

In summary, in this experiment three following calculations will be performed:

1. # hf/6-31g*
2. # mp2/6-31g*
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The type of calculations is also specified in the route section with keywords ‘opt’ and ‘freq’. The ‘opt’ keyword means ‘optimization’; the program is requested to optimize molecular geometry, i.e., to find the structure with the lowest potential energy. The ‘freq’ keyword specifies calculations of vibrational frequencies. These two keywords should be present in all three calculations.

The **title section** includes an arbitrary comment describing your calculations. It will be also found in the output file.

The **charge and multiplicity** section indicates molecular charge and multiplicity. For the neutral molecules, the charge is specified as ‘0’. The multiplicity is the number of unpaired electrons in the molecule + 1, i.e., ‘1’ for singlet, ‘2’ for doublet, ‘3’ for triplet, etc.

The **molecular specification** section is used to input initial molecular geometry. It is specified in the form of atomic Cartesian coordinates or a so-called z-matrix, which shows interatomic distances, bond angles, and torsional angles. In the case of a diatomic molecule, students need to specify only the two atoms comprising the molecule and the distance between them:

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Li
H   1   R
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Here, the first atom in the molecule is lithium ‘Li’ and the second is hydrogen ‘H’ and the Li-H distance is designated with the variable ‘R’, which will be optimized during the calculations. The initial values for this variable is given (in angstrom) after a blank line:

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After the input is prepared, click the ‘Run’ button to submit calculations. You will then be prompted to specify a name for the output file and the calculations will run.

As the calculations are completed, open the output file with a word processor (MsWord). The output file contains a lot of information including molecular potential energy calculated for each optimization step, wave function expressed as linear combination of atomic orbitals in the basis set, orbital energies, atomic electric charges, etc. The required information is the optimized interatomic distance and the vibrational frequency, which are given as follows:

```
-- Stationary point found.
                   ----------------------------
                   !   Optimized Parameters   !
                   ! (Angstroms and Degrees)  !
 -----------------------          -----------------------
 ! Name  Definition          Value        Derivative Info.        !
 --------------------------------------------------------------------------------
 ! R1    R(1,2)              1.6209       -DE/DX =    0.           !
 --------------------------------------------------------------------------------
```

and

```
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                  1
                 SG
 Frequencies --  1399.1094
 Red. masses --     1.1293
 Frc consts  --     1.3024
 IR Inten    --   117.6770
 Raman Activ --     0.0000
 Depolar     --     0.0000
 Atom AN      X      Y      Z
   1   3     0.00   0.00   0.14
   2   1     0.00   0.00  -0.99
```

For LiH, these results show that the optimal Li-H bond length is 1.6209 Å and the vibrational frequency is 1399 cm^{-1}.

The lab report should include the results (interatomic distances and vibrational frequencies) of the calculations using three different methods, HF/6-31g*, MP2/6-31g*, and B3LYP/6-31g*. In the discussion, compare your calculated results with the literature data (experimental and theoretical) and compare the accuracy of different methods versus experimental values. Also sketch the molecular orbital energy diagram for your molecule, deduce its ground state electronic configuration, and multiplicity. Compare the deduced electronic configuration with the calculated one – the GAUSSIAN output provides calculated energies of the occupied and vacant molecular orbitals.

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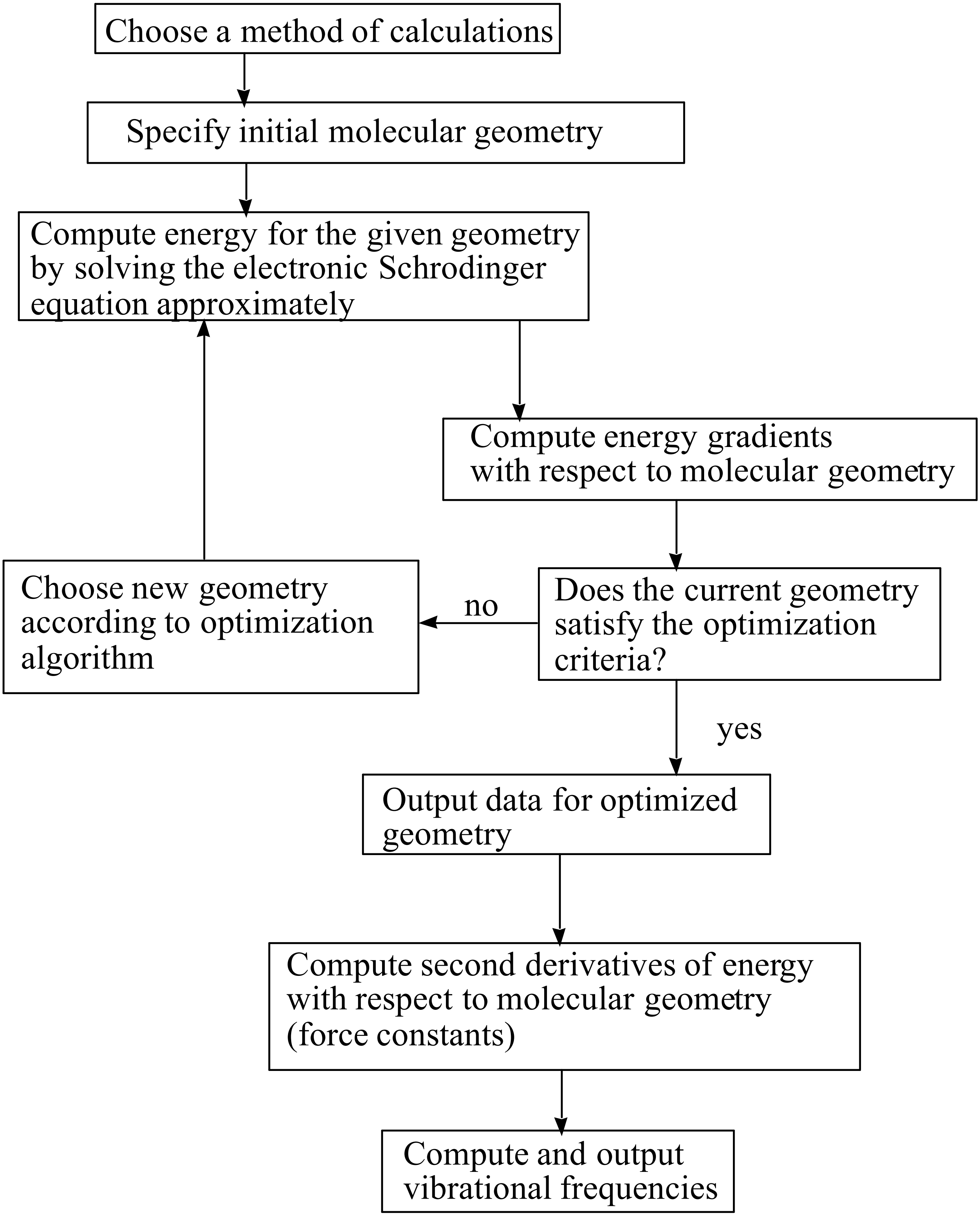
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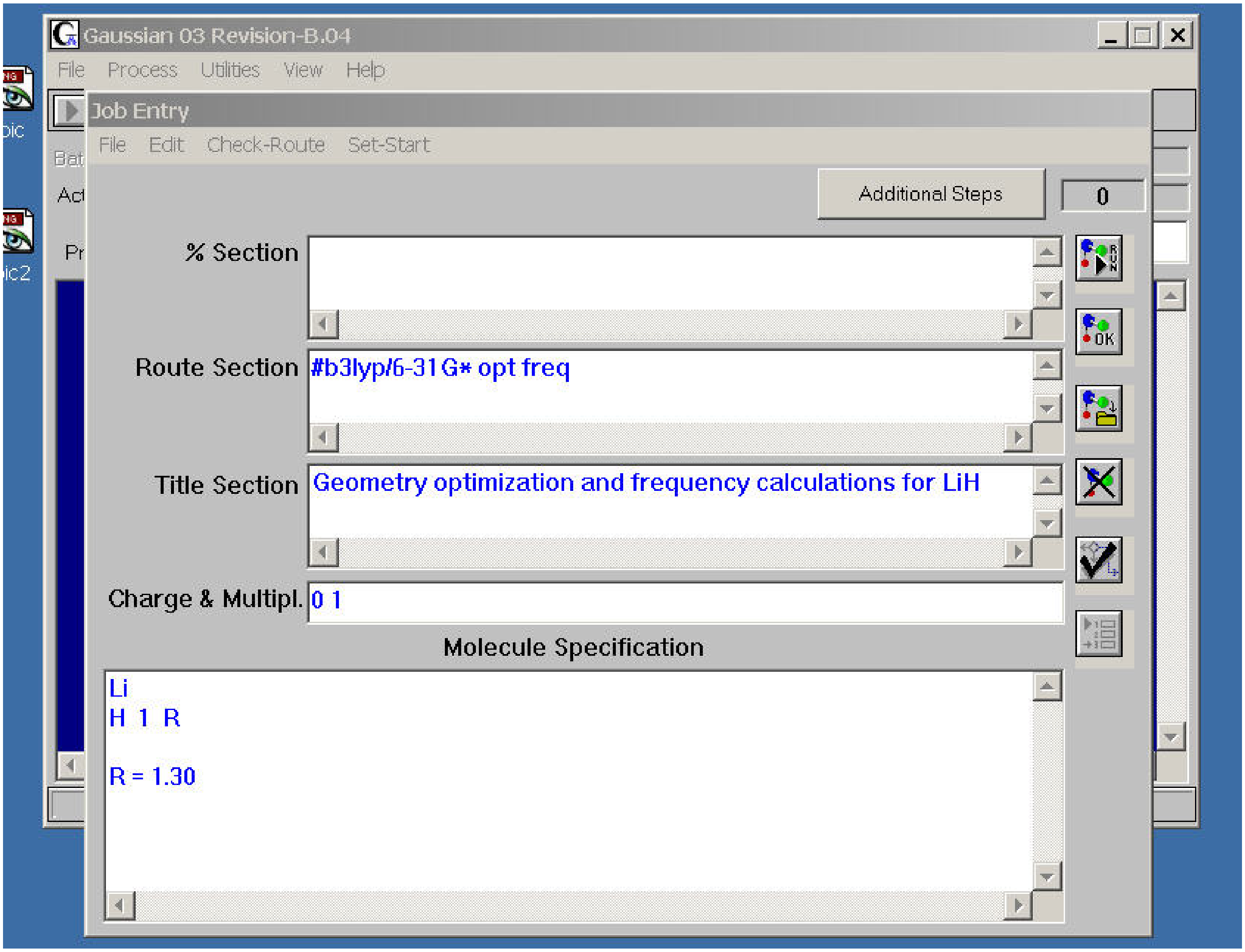

Route Section: #b3lyp/6-31G* opt freq

Title Section: Geometry optimization and frequency calculations for LiH

Charge & Multipl.: 0 1

Molecule Specification

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```
-- Stationary point found.
                         ----------------------------
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 -----------------------              ------------------------
 ! Name  Definition            Value        Derivative Info.          !
 ---------------------------------------------------------------------------
 ! R1    R(1,2)              1.6209      -DE/DX =    0.              !
 ---------------------------------------------------------------------------
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```
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 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
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                     SG
 Frequencies --  1399.1094
 Red. masses --     1.1293
 Frc consts  --     1.3024
 IR Inten    --   117.6770
 Raman Activ --     0.0000
 Depolar     --     0.0000
 Atom AN      X      Y      Z
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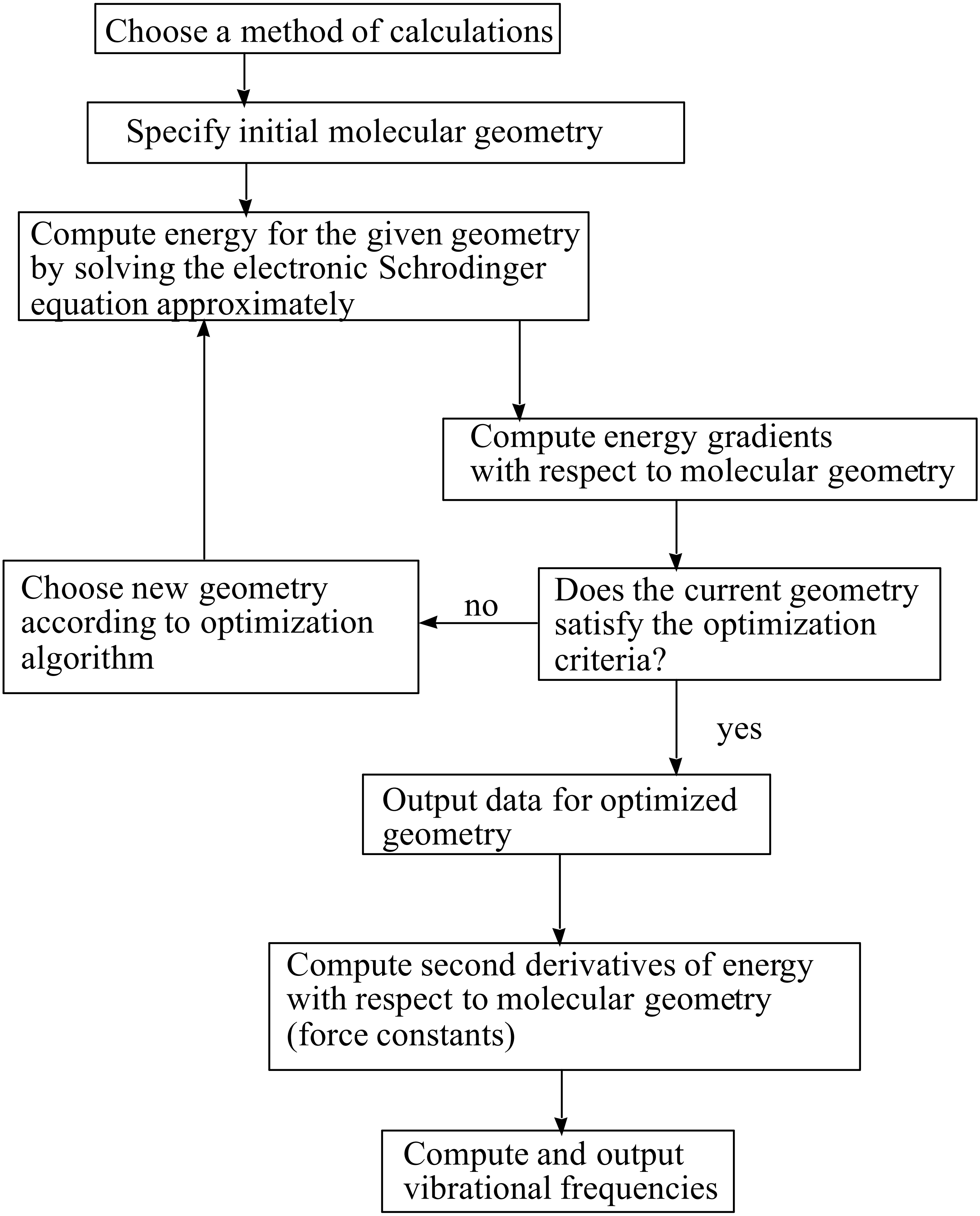
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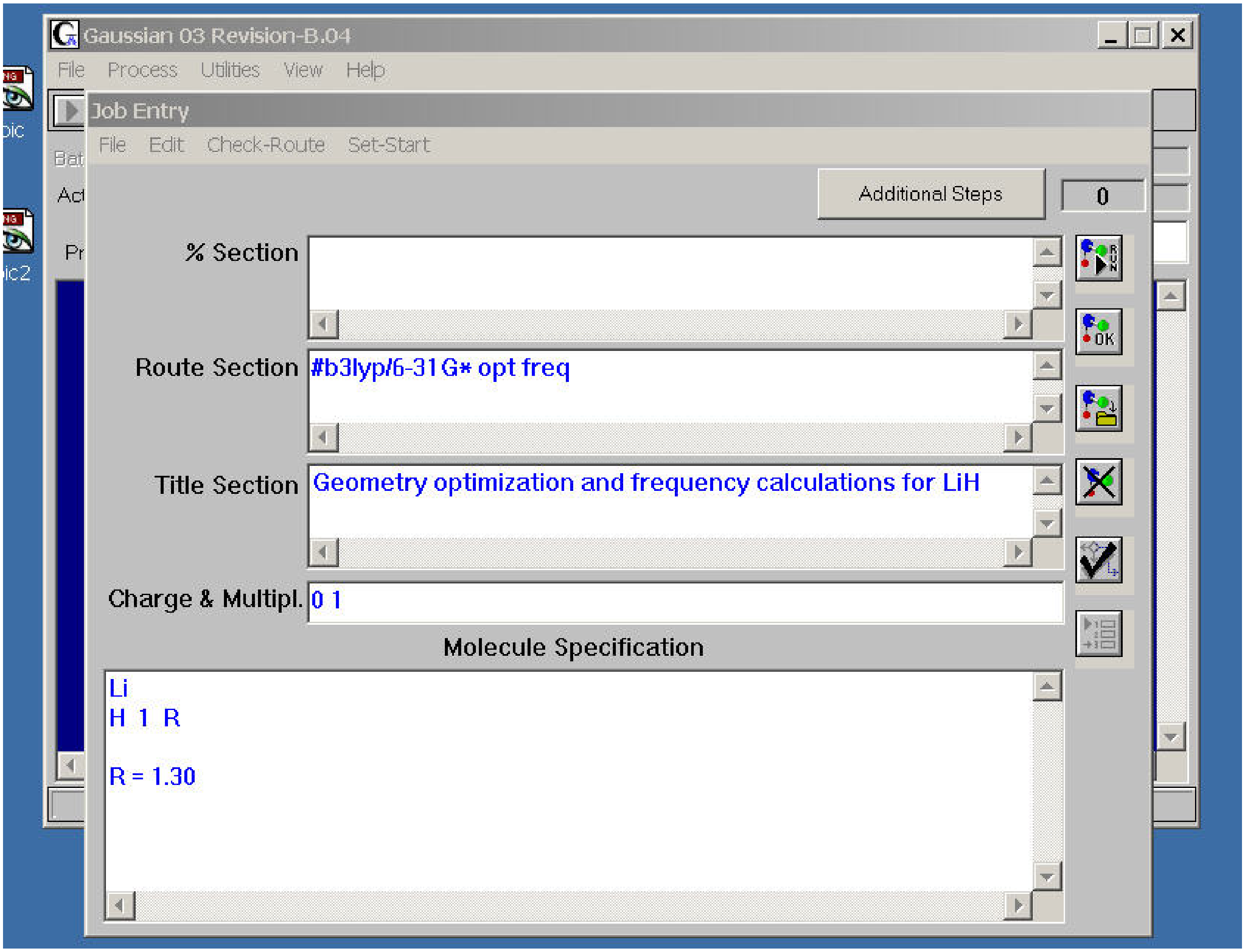
‘Experimental’

Chose a diatomic molecule for calculations. It is recommended that it was the molecule for which the student carried out literature search in the PChem Lab I CHM3410L course. Submit GAUSSIAN program on the PC in the PChem Lab and type in the input data that include the method of calculations, molecular charge and multiplicity, and initial molecular geometry:



Route Section: #b3lyp/6-31G* opt freq

Title Section: Geometry optimization and frequency calculations for LiH

Charge & Multipl.: 0 1

```
Li
H  1  R

R = 1.30
```

Route section specifies the method and the type of calculations. The method is a quantum chemical procedure to be used to find an approximate solution for the electronic Schrödinger equation and the basis set for molecular wave function. The calculations should be carried out employing three different methods:

1) The Hartree-Fock method ‘HF’: this is the simplest ‘ab initio’ (from the first principles) method, in which the molecular many-electron wave function is expressed as a determinant composed from one-electron wave functions of all electrons in the molecule. The HF method is time-efficient but rather approximate, since it does not take into account the correlation between motion of different electrons in the molecule (electronic correlation): each electron is assumed to be moving in an average field created by all other electrons (and by nuclei).

2) The Møller-Plesset second-order perturbation theory method (MP2): this is the cheapest and most efficient method, which takes into account electronic correlation to some extent. It should be more accurate than HF.

3) Density functional B3LYP method. In density functional theory (DFT), the electronic energy is expressed as a functional of electron density (square of the wave function). This group of methods is the most popular and fast developing in quantum chemistry in recent years; they take into account electronic correlation but are as time-efficient as HF.

The basis set is specified after the ‘/’. The need to have a basis set in the GAUSSIAN calculations is related to the fact that the wave function for each electron in the molecule is expressed as a linear combination of atomic orbitals, i.e. the orbitals of the hydrogen-atom type. The basis set specifies how many hydrogen-atom type s, p, d, etc., orbitals are included. In these calculations, students will use the 6-31G* basis set.

In summary, in this experiment three following calculations will be performed:

1. # hf/6-31g*
2. # mp2/6-31g*
3. # b3lyp/6-31g*

The type of calculations is also specified in the route section with keywords ‘opt’ and ‘freq’. The ‘opt’ keyword means ‘optimization’; the program is requested to optimize molecular geometry, i.e., to find the structure with the lowest potential energy. The ‘freq’ keyword specifies calculations of vibrational frequencies. These two keywords should be present in all three calculations.

The **title section** includes an arbitrary comment describing your calculations. It will be also found in the output file.

The **charge and multiplicity** section indicates molecular charge and multiplicity. For the neutral molecules, the charge is specified as ‘0’. The multiplicity is the number of unpaired electrons in the molecule + 1, i.e., ‘1’ for singlet, ‘2’ for doublet, ‘3’ for triplet, etc.

The **molecular specification** section is used to input initial molecular geometry. It is specified in the form of atomic Cartesian coordinates or a so-called z-matrix, which shows interatomic distances, bond angles, and torsional angles. In the case of a diatomic molecule, students need to specify only the two atoms comprising the molecule and the distance between them:

```
Li
H  1  R
```

Here, the first atom in the molecule is lithium ‘Li’ and the second is hydrogen ‘H’ and the Li-H distance is designated with the variable ‘R’, which will be optimized during the calculations. The initial values for this variable is given (in angstrom) after a blank line:

```
R = 1.30
```

After the input is prepared, click the ‘Run’ button to submit calculations. You will then be prompted to specify a name for the output file and the calculations will run.

As the calculations are completed, open the output file with a word processor (MsWord). The output file contains a lot of information including molecular potential energy calculated for each optimization step, wave function expressed as linear combination of atomic orbitals in the basis set, orbital energies, atomic electric charges, etc. The required information is the optimized interatomic distance and the vibrational frequency, which are given as follows:

```
-- Stationary point found.
                       ----------------------------
                       !   Optimized Parameters   !
                       ! (Angstroms and Degrees)  !
 -----------------------                          ------------------------
 ! Name  Definition             Value          Derivative Info.          !
 --------------------------------------------------------------------------
 ! R1    R(1,2)                 1.6209         -DE/DX =    0.            !
 --------------------------------------------------------------------------
```

and

```
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                    1
                   SG
 Frequencies --  1399.1094
 Red. masses --     1.1293
 Frc consts  --     1.3024
 IR Inten    --   117.6770
 Raman Activ --     0.0000
 Depolar     --     0.0000
 Atom AN      X      Y      Z
   1   3     0.00   0.00   0.14
   2   1     0.00   0.00  -0.99
```

For LiH, these results show that the optimal Li-H bond length is 1.6209 Å and the vibrational frequency is 1399 cm^{-1}.

The lab report should include the results (interatomic distances and vibrational frequencies) of the calculations using three different methods, HF/6-31g*, MP2/6-31g*, and B3LYP/6-31g*. In the discussion, compare your calculated results with the literature data (experimental and theoretical) and compare the accuracy of different methods versus experimental values. Also sketch the molecular orbital energy diagram for your molecule, deduce its ground state electronic configuration, and multiplicity. Compare the deduced electronic configuration with the calculated one – the GAUSSIAN output provides calculated energies of the occupied and vacant molecular orbitals.