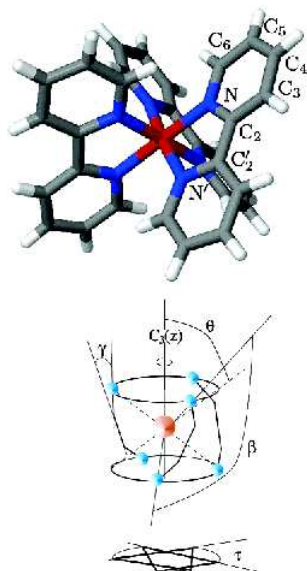


# Time-Dependent Density-Functional Theory for the Calculation of Molecular Electronic Excited States

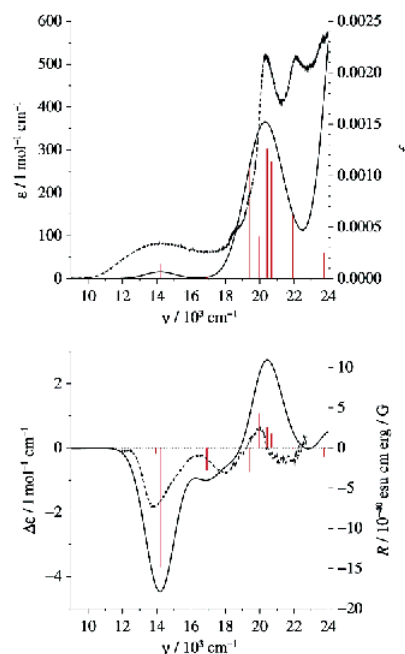
## 2nd Year Masters, Theoretical Chemistry

Mark E. CASIDA

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**Figure 2.** Atom labeling used for the  $D_3$   $[\text{Co}(\text{bpy})_3]^{2+}$  complex (top) and angles characterizing the arrangement of the ligands around the cobalt center (bottom):  $\beta$  is the bite angle,  $\gamma$  the dihedral angle between the ligand moieties,  $\tau$  the twist angle, and  $\theta$  the angle between the z axis and the generator of the cone on which the nitrogen atoms are located.



**Figure 4.** Calculated absorption (top) and CD (bottom) spectra of LS A- $[\text{Co}(\text{bpy})_3]^{2+}$ . The experimental single-crystal absorption and CD spectra of  $[\text{Co}(\text{bpy})_3][\text{LiF}(\text{ox})_3]$ , recorded at 11 and 15 K, respectively, are shown (dashed lines) for comparison.

The cobalt(II)tris(2,2'-biypiridine) complex and the experimental absorption and circular dichroism spectra of its high-spin  ${}^2E(t_{2g}^6 e_g^1)$  state compared with those calculated from TDDFT. [Taken from the publication of A. Vargas *et al.*, J. Chem. Theory Comput. **2**, 1342 (2006).]



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# Preface

In 2007 Anne Milet, coordinator for the 2nd year Masters label in Theoretical Chemistry in Grenoble, graciously requested that I teach a course of 10 hour or so in one of my areas of expertise, time-dependent density-functional theory (TDDFT). These notes are the result.

The success of TDDFT in recent years has been rather explosive as attested to by Fig. 1. Most applications of TDDFT are in the form of the linear response equations for treating molecular excited states. More than a decade ago, I wrote an article describing what are now sometimes known as “Casida’s equations” for calculating excited states from TDDFT. The importance of this article is that it explained TDDFT to *ab initio* quantum chemists and explained linear response theory to DFT chemists. (The two groups were rather separate at that time.) *Grosso modo* before my article most quantum chemists thought that DFT could not treat excited states. After my article, that attitude changed rapidly. Today TDDFT has become (with some notable exceptions) the single-determinant method of choice for the treatment of the electronic excited states of large molecules. But the method is far from being a black box! On the contrary, proper training is needed in order to use the method correctly. That is why courses such as this one are necessary.

There are now a number of review articles on the subject of TDDFT (see the end of this preface) and some are written by me [1, 2, 3, 4]. There is also a recent book on the subject which resulted from two summer schools on TDDFT.[5] So is there really a need for another course on TDDFT? Given the advanced level of background knowledge required by most of the review articles, I think that there rather is a need for a course on TDDFT at a level more accessible to second year Masters students in Chemical Physics/Physical Chemistry. For this reason, much of these notes concerns subjects which are not strictly speaking TDDFT, but which are important for understanding how TDDFT is applied to treat electronic excited states. Only after having treated these aspects are the formalism and the practical problems of TDDFT presented.

Rumor has it that the courses (or some of them) in this program will be taught in English in the future in order to satisfy the needs of an increasingly international group of students. Having spent 10 years of my life in Montréal (where language is often as much a political statement as a means of communication) I am very sensitive to the question of French versus English. So here is a very Canadian document, available in both languages.

## Some Reviews

### 2005-2007

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“Excited states from time-dependent density functional theory”
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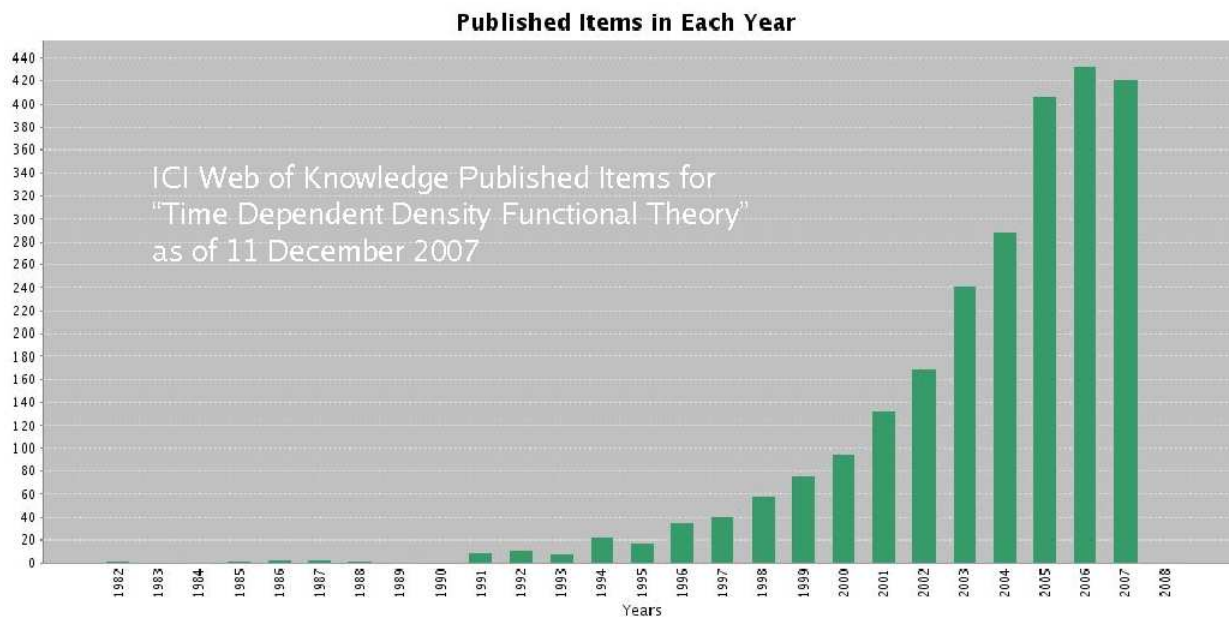


Figure 1: Growth of the number of articles referring to TDDFT according to the *Web of Science*.

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“Jacob’s ladder for time-dependent density-functional theory: Some rungs on the way to photochemical heaven”
- N.T. Maitra, K. Burke, H. Appel, E.K.U. Gross and R. van Leeuwen, in *Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr*, K.D. Sen, ed(s), (World Scientific, 2002) p. 1186-1225.  
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# Units

This section addresses the inevitable question of choice of units. While the official tendency is to recommend the use of Système International (SI) units, the tendency in electromagnetism is still the use of non SI units, such as Gaussian units. Furthermore theorists overwhelmingly use atomic units (AU), a system based upon Gaussian, rather than SI, units. Gaussian units will be used in chapter ?? where I try to make a direct link with experiment. Thus the mass of an electron  $m_e$ , its charge  $e$ , and  $\hbar$  (Planck's constant multiplied by  $2\pi$ ) will be explicitly displayed. On the other hand, in the more theoretical chapters (chapters ?? and ??), I will make use of atomic units. The objective of this little section is to take stock of these different systems of units.

Let us first consider the classical expression for the total energy of a molecule. For  $N$  electrons and  $M$  nuclei, a good approximation for the energy is,

$$\begin{aligned}
 E_{\text{totale}} &= \sum_{I=1}^M \frac{|p_I|^2}{2m_I} + \sum_{I=1}^M \sum_{J=I+1}^M \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \\
 &+ \sum_{i=1}^N \frac{|p_i|^2}{2m_e} + \sum_{i=1}^N \sum_{j=1}^M \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\
 &- \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|}, \tag{1}
 \end{aligned}$$

where  $m_e$  is the mass of the electron and  $e = |e|$  is (minus) the charge of an electron.

One thing which can cause problems is the question of unities. We will use Gaussian units in Eq. (1). In this system of electromagnetic units, the force between two charges is given by

$$\begin{aligned}
 \vec{F} &= \frac{Q_1 Q_2}{r^2} \hat{r} \\
 &= \frac{Q_1 Q_2}{r^3} \vec{r}, \tag{2}
 \end{aligned}$$

where

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{3}$$

The potential corresponding to this force is given by

$$V = -\frac{Q_1 Q_2}{r}, \tag{4}$$

because of the definition

$$\begin{aligned}
 \vec{F} &= -\vec{\nabla} V \\
 &= -\begin{pmatrix} \partial V / \partial x \\ \partial V / \partial y \\ \partial V / \partial z \end{pmatrix}, \tag{5}
 \end{aligned}$$

where

$$\vec{\nabla} = \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{pmatrix} \quad (6)$$

is the gradient operator. In the Gaussian system, we use the units centimeter (distance), gram (mass), second (time), and stat coulomb or electrostatic unit (esu, charge).

On the other hand, système international (SI) units are often those officially recommended by journals and for teaching (though the tendency in some areas of research is not to follow these recommendations.) In SI units, distance is measured in meters, mass in kilograms, time in seconds, and charge in coulombs. It is important to understand the the unit of charge does not have the same dimensionality in Gaussian and SI units. It is thus not too surprising that there is a constant with units which enters into the SI expression for the force between two charges,

$$\vec{F} = \frac{Q'_1 Q'_2}{4\pi\epsilon_0 r^2} \hat{r}, \quad (7)$$

where  $\epsilon_0 = 8,854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2$  is the permativity of free space. In comparing with Eqs. (2) and (7), we see that

$$Q' = \sqrt{4\pi\epsilon_0} Q, \quad (8)$$

a conversion factor between the two systems of units which is good enough for this course. The potential corresponding to the force given in Eq. (7) is in given in SI units,

$$V = -\frac{Q'_1 Q'_2}{4\pi\epsilon_0 r}. \quad (9)$$

Finally the system of atomic units (AU) is also very much used in the field of quantum chemistry. The UA system is based upon the Gaussian system discussed above. It further choses  $\hbar$ , the absolute value of the charge of an electron, and the mass of an electron to be equal to one atomic unit. Alternatively (and more correctly) by using AU's we have decided to express all quantities in terms of only the 3 basic quantities  $e$ ,  $m_e$ , and  $\hbar$ . This leads us to the following table:

quantity	AU	name
angular momentum	$\hbar$	
charge	$e$	
mass	$m_e$	
distance	$a_0 = \hbar^2/m_e e^2$	bohr
energy	$E_h = e^2/a_0 = m_e e^4/\hbar^2$	hartree
(linear) momentum	$e^2/\hbar$	
	etc.	

Note that only some AU have names, such as *bohr* for distance and *hartree* for energy.

# Chapter 1

## Fundamentals of DFT and TDDFT

This chapter is an introduction to density-functional theory (DFT) and to time-dependent density-functional theory (TDDFT). In both cases, the idea is to replace the wave function  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ , which is a complicated function of  $3N$  spatial coordinates and  $N$  spin coordinates, with the density  $\rho(\mathbf{x})$ , which is a simpler object which depends only upon the three coordinates  $(x, y, z)$  and the spin  $\sigma$ .

At first thought replacing  $\Psi$  by  $\rho$  would seem to mean losing large amounts of information needed for practical calculations. The importance of the Hohenberg-Kohn theorems in DFT is that the ground state energy may be determined in principle by minimizing a functional of the density, which is a simpler object than the wavefunction. Unfortunately there is no practical exact realization of this functional and so approximations are necessary. In general these approximations are functions of the density and its gradients and are manipulated using the calculus of variations which will be presented here. The emphasis is on the local approximation, which is the simplest practical approximation.

The limitation of ordinary DFT to the ground stationary state is really disappointing if one wishes to calculate optical properties or to treat excited states. TDDFT was invented to overcome this limitation. The Runge-Gross theorems serve a role in TDDFT which is analogous to the Hohenberg-Kohn theorems in DFT. The adiabatic approximation is local in time and plays the role of the simplest practical approximation.

### 1.1 DFT

#### I. The Two Hohenberg-Kohn Theorems

These two theorems are the basis of modern density-functional theory (DFT). They respond in the affirmative to the question:

Can we eliminate  $\Psi$ ?

Theorem. Any function  $\rho$  is an  $N$ -representable charge density provided that

i) 
$$\rho(\vec{r}) \geq 0; \forall \vec{r} \tag{1.1}$$

ii) 
$$\int \rho(\vec{r}) d\vec{r} = N \tag{1.2}$$

Proof. Given in certain articles, notably one by John E. Harriman.

♡

But is  $\rho$  sufficient for determining  $E$ ? Hohenberg and Kohn showd that the answer is “yes”!

Theorem (HK1) The groundstate charge density for a system with a nondegenerate ground state is determines the external potential up to an additive constant.

Remark

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_{i=1,N} \nabla_i^2}_{\hat{T}} + \underbrace{\sum_{i=1,N} v_{\text{ext}}(\vec{r}_i)}_{V_{\text{ext}}} + \underbrace{\sum_{i,j=1,N}^{(i<j)} \frac{1}{r_{ij}}}_{V_{ee}}, \quad (1.3)$$

- $\hat{T}$  : electron kinetic energy
- $V_{\text{ext}}$  : nuclear attraction and/or interaction with an applied electric field
- $V_{ee}$  : electron repulsion

Proof Suppose that there are two systems, both with nondegenerate ground states, and the same charge density, but different potentials:

$$\begin{aligned} v_{\text{ext}}^{(1)} &\rightarrow \Psi_1 \rightarrow \rho \\ v_{\text{ext}}^{(2)} &\rightarrow \Psi_2 \rightarrow \rho \\ v_{\text{ext}}^{(1)} - v_{\text{ext}}^{(2)} &\neq \text{constant}. \end{aligned} \quad (1.4)$$

Look for a contradiction!

$$\Psi_1 \neq \Psi_2 \quad (1.5)$$

since

$$v_{\text{ext}}^{(1)} - v_{\text{ext}}^{(2)} \neq \text{constant}. \quad (1.6)$$

Because of the variational principle,

$$\begin{aligned} E_1 &= \langle \Psi_1 | \hat{T} | \Psi_1 \rangle + \int v_{\text{ext}}^{(1)}(\vec{r}) \rho(\vec{r}) d\vec{r} \\ &< \langle \Psi_2 | \hat{T} | \Psi_2 \rangle + \int v_{\text{ext}}^{(1)}(\vec{r}) \rho(\vec{r}) d\vec{r} \\ E_2 &= \langle \Psi_2 | \hat{T} | \Psi_2 \rangle + \int v_{\text{ext}}^{(2)}(\vec{r}) \rho(\vec{r}) d\vec{r} \\ &< \langle \Psi_1 | \hat{T} | \Psi_1 \rangle + \int v_{\text{ext}}^{(2)}(\vec{r}) \rho(\vec{r}) d\vec{r}. \end{aligned} \quad (1.7)$$

Thus we have,

$$\begin{aligned} \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle &< \langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle \\ \langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle &< \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle, \end{aligned} \quad (1.8)$$

which is a contradiction! Hence

$$\begin{aligned}
 \rho &\rightarrow N, v_{\text{ext}} + \text{constant} \\
 &\rightarrow \hat{H} \\
 &\rightarrow \Psi \\
 &\text{etc.}
 \end{aligned} \tag{1.9}$$

♡

Theorem (HK2) The electronic energy satisfies the variational condition, L'énergie électronique du système satisfait la condition variationnelle,

$$E_{\text{exacte}} \leq F[\rho] + \int v_{\text{ext}}(\vec{r})\rho(\vec{r}) d\vec{r}, \tag{1.10}$$

where  $F[\rho]$  is a universal functional of the density. It is universal in the sense that it is independent of  $v_{\text{ext}}$ . Equality means that we also have  $\rho_{\text{exacte}}$ .

Remark: A functional is a function of a function. We use square brackets [ ] to distinguish a functional from a simple function.

Proof

$$\begin{aligned}
 E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} | \Psi \rangle \\
 &= \min_{\rho} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} | \Psi \rangle \\
 &= \min_{\rho} \left[ \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle}_{F[\rho]} + \int v_{\text{ext}}(\vec{r})\rho(\vec{r}) d\vec{r} \right].
 \end{aligned} \tag{1.11}$$

The minimum is found when we have found the ground state wave function  $\Psi$  and hence  $\rho$  for the ground state.

♡

It is hoped that, by knowing  $F[\rho]$ , we can determine  $E_{\text{exacte}}$  and  $\rho_{\text{exacte}}$ , without ever calculating  $\Psi$ . But the formula for  $F[\rho]$  requires that we calculate  $\Psi$ ! We thus have an existence theorem for  $F[\rho]$ , but we still need to find approximations for  $F[\rho]$  which avoid calculating  $\Psi$ . How?

## II. Homogeneous Electron Gas (HEG)

There is at least one model system which is completely characterized by its density. Thus every property is a function of  $\rho$ .

Definition. The HEG (also known as “jellium”) is made up of  $N$  electrons in a box of volume  $V = \ell^3$  with a positive background density of  $\rho = N/V$ . We let  $\ell \rightarrow \infty$ , while keeping  $\rho$  constant.

The total energy is given by

$$\begin{aligned}
 E &= T_s + \int v_{\text{ext}}(\vec{r})\rho(\vec{r}) d\vec{r} \\
 &+ \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \\
 &+ E_{xc} + E_b,
 \end{aligned} \tag{1.12}$$

where

$$E_b = +\frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \tag{1.13}$$

is the background energy. As

$$v_{\text{ext}}(\vec{r}) = - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}', \tag{1.14}$$

we have that

$$E = T_s + E_{xc}. \tag{1.15}$$

We would like to find expressions for the energy densities,

$$\begin{aligned}
 t_s &= T_s/V \\
 \rho\epsilon_x &= E_x/V \\
 \rho\epsilon_c &= E_c/V.
 \end{aligned} \tag{1.16}$$

The results are traditionally expressed in terms of the Wigner-Seitz radius, which is the radius of a sphere containing the charge of one electron — that is,

$$\begin{aligned}
 \frac{4\pi}{3}r_s^3 &= \frac{1}{\rho} \\
 &\Rightarrow \\
 r_s &= \left(\frac{3}{4\pi\rho}\right)^{1/3}.
 \end{aligned} \tag{1.17}$$

For the HEG, the orbitals are plane waves

$$\psi_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \tag{1.18}$$

with boundary conditions (quantization),

$$\begin{aligned}
 k_x &= \frac{2\pi}{\ell} n_x \\
 k_y &= \frac{2\pi}{\ell} n_y \\
 k_z &= \frac{2\pi}{\ell} n_z.
 \end{aligned} \tag{1.19}$$

The density of states (DOS) is thus

$$d\vec{n} = \frac{V}{8\pi^3} d\vec{k}. \tag{1.20}$$

To determine the “Fermi momentum” (that is the HOMO),

$$\begin{aligned}
N &= 2 \int d\vec{n} \\
&= \frac{V}{4\pi^3} \int d\vec{k} \\
&= \frac{V}{\pi^2} \int_0^{k_F} k^2 dk \\
&= \frac{V}{3\pi^2} k_F^3 \\
&\Rightarrow \\
k_F &= (3\pi^2 \rho)^{1/3}.
\end{aligned} \tag{1.21}$$

Kinetic Energy Density. We can now calculate the kinetic energy density,

$$t_s = \frac{2}{V} \int \int \psi_{\vec{k}}^*(\vec{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_{\vec{k}}(\vec{r}) d\vec{n} d\vec{r}. \tag{1.22}$$

As

$$\nabla^2 \psi_{\vec{k}}(\vec{r}) = -k^2 \psi_{\vec{k}}(\vec{r}) \tag{1.23}$$

and

$$\psi_{\vec{k}}^*(\vec{r}) \psi_{\vec{k}}(\vec{r}) = \frac{1}{V}, \tag{1.24}$$

we have

$$\begin{aligned}
t_s &= \frac{1}{V^2} \int \int k^2 d\vec{n} d\vec{r} \\
&= \frac{1}{V} \int k^2 d\vec{n} \\
d\vec{n} &= \frac{V}{8\pi^3} \int d\vec{k} \\
&= \frac{V}{2\pi^2} \int k^2 dk \\
t_s &= \frac{1}{2\pi^2} \int k^4 d\vec{k} \\
&= \frac{k_F^5}{10\pi^5} \\
t_s &= \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}.
\end{aligned} \tag{1.25}$$

Exchange Energy Density. The quantity  $\rho\epsilon_x$  may be obtained analytically but its derivation is a bit complicated. The result is

$$\rho\epsilon_x = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{4/3}. \tag{1.26}$$

Correlation Energy Density. It is almost certainly impossible to obtain  $\rho\epsilon_c$  analytically. Wigner suggested as a first approximation,

$$\epsilon_c \approx -\frac{0,44}{7,8 + r_s}. \tag{1.27}$$

Today we use parameterized fits to Ceperley and Alder’s Quantum Monte Carlo calculations on the HEG. The expressions, which are not simple, may be found in the references Refs. [6, 7, 8].

### III. Local Approximations

#### A. Definition of a Local Approximation

If  $U$  is a global energy (e.g. kinetic, exchange, ...) and

$$U = \int u(\vec{r}) d\vec{r}, \tag{1.28}$$

the function  $u$  is an energy density for  $U$ . According to Hohenbert and Kohn,

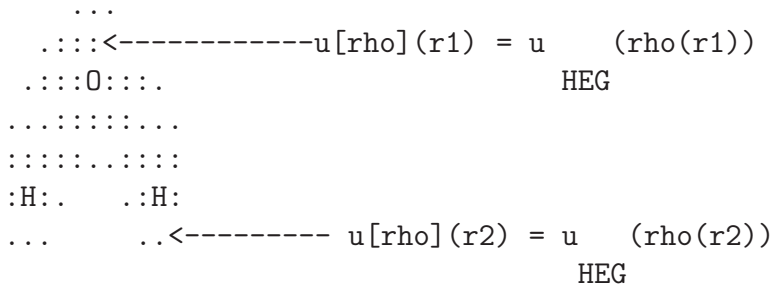
$$U[\rho] = \int u[\rho](\vec{r}) d\vec{r}. \tag{1.29}$$

For the HEG,  $\rho$  is a constant. Hence

$$\begin{aligned} U(\rho) &= u(\rho)V \\ &\Rightarrow \\ u(\rho) &= \frac{U(\rho)}{V}. \end{aligned} \tag{1.30}$$

The local approximation for  $U$  is given by

$$\begin{aligned} U &= \int u[\rho](\vec{r}) d\vec{r} \\ &\approx \int u_{\text{HEG}}(\rho(\vec{r})) d\vec{r}. \end{aligned} \tag{1.31}$$



SCHMATIC OF THE LOCAL APPROXIMATION

#### Thomas-Fermi

$$\begin{aligned} E_{\text{TF}}[\rho] &= C_{\text{TF}} \int \rho^{5/3}(\vec{r}) d\vec{r} \\ &+ \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} \\ &+ \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2. \end{aligned} \tag{1.32}$$

#### Thomas-Fermi-Dirac

$$E_{\text{TFD}}[\rho] = E_{\text{TF}}[\rho] - C_x \int \rho^{4/3}(\vec{r}) d\vec{r}. \tag{1.33}$$

Local approximations shouldd work for a slightly perturbed HEG but not necessarily for a molecule.



“We do not expect an accurate description of chemical bonding.”

W. Kohn et L.J. Sham, Phys. Rev. **140**, A1133 (1965).

## B. The Calculus of Variations

This is a generalization for functionals of the ideas of Newton and Leibnitz.

$$\begin{aligned} f(\vec{r} + d\vec{r}) - f(\vec{r}) &= df = \sum \frac{\partial f}{\partial r_i} dr_i \\ F[\rho + \delta\rho] - F[\rho] &= \delta F = \int \frac{\delta F}{\delta\rho(\vec{r})} \delta\rho(\vec{r}) d\vec{r}. \end{aligned} \quad (1.34)$$

• If

$$F[\rho] = \int f(\rho(\vec{r})) d\vec{r}, \quad (1.35)$$

then

$$\begin{aligned} \delta F &= F[\rho + \delta\rho] - F[\rho] \\ &= \int [f(\rho(\vec{r} + \delta\rho(\vec{r})) - f(\rho(\vec{r}))] d\vec{r} \\ &= \int \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho(\vec{r})} \delta\rho(\vec{r}) d\vec{r}. \end{aligned} \quad (1.36)$$

So

$$\frac{\delta F}{\delta\rho(\vec{r})} = \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho(\vec{r})}. \quad (1.37)$$

• For

$$T_W[\rho] = \frac{1}{8} \int \frac{\vec{\nabla}\rho(\vec{r}) \cdot \vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})} d\vec{r}, \quad (1.38)$$

and using the fact that,

$$\begin{aligned} \frac{1}{1 + \delta\rho} &= \frac{1}{\rho} \left( \frac{1}{1 + \frac{\delta\rho}{\rho}} \right) \\ &= \frac{1}{\rho} \left( 1 - \frac{\delta\rho}{\rho} \right), \end{aligned} \quad (1.39)$$

we have

$$\begin{aligned} T_W[\rho + \delta\rho] - T_W[\rho] &= \frac{1}{8} \int \frac{\vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r})) \cdot \vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r}))}{\rho(\vec{r}) + \delta\rho(\vec{r})} d\vec{r} \\ &= \frac{1}{8} \int \frac{\vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r})) \cdot \vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r}))}{\rho(\vec{r})} d\vec{r} \\ &\quad - \frac{1}{8} \int \frac{\vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r})) \cdot \vec{\nabla}(\rho(\vec{r}) + \delta\rho(\vec{r}))}{\rho^2(\vec{r})} d\vec{r} \\ &= T_W[\rho] + \frac{1}{4} \int \frac{\vec{\nabla}\delta\rho(\vec{r}) \cdot \vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})} d\vec{r} - \frac{1}{8} \int \frac{\vec{\nabla}\rho(\vec{r}) \cdot \vec{\nabla}\rho(\vec{r})}{\rho^2(\vec{r})} \delta\rho(\vec{r}) d\vec{r} \end{aligned}$$

$$\begin{aligned}
&= T_W[\rho] - \frac{1}{4} \int \frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})} \delta \rho(\vec{r}) d\vec{r} - \frac{1}{8} \int \frac{\vec{\nabla} \rho(\vec{r}) \cdot \vec{\nabla} \rho(\vec{r})}{\rho^2(\vec{r})} \delta \rho(\vec{r}) d\vec{r} \\
&\Rightarrow \\
\frac{\delta T_W[\rho]}{\delta \rho(\vec{r})} &= -\frac{1}{4} \frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})} - \frac{1}{8} \frac{\vec{\nabla} \rho(\vec{r}) \cdot \vec{\nabla} \rho(\vec{r})}{\rho^2(\vec{r})}. \tag{1.40}
\end{aligned}$$

• For

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \tag{1.41}$$

we have

$$\begin{aligned}
J[\rho + \delta \rho] &= \frac{1}{2} \int \int \frac{(\rho(\vec{r}_1) + \delta \rho(\vec{r}_1)) (\rho(\vec{r}_2) + \delta \rho(\vec{r}_2))}{r_{12}} d\vec{r}_1 d\vec{r}_2 \\
&= J[\rho] + \int \int \frac{\rho(\vec{r}_1)}{r_{12}} d\vec{r}_1 \delta \rho(\vec{r}_2) d\vec{r}_2 \\
&\Rightarrow \\
\frac{\delta J[\rho]}{\delta \rho(\vec{r})} &= \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \tag{1.42}
\end{aligned}$$

• A very general formula is

$$\begin{aligned}
F[\rho] &= \int f(x, \rho, \rho^{(1)}, \rho^{(2)}, \dots, \rho^{(n)}) dx \\
&\Rightarrow \\
\frac{\delta F}{\delta \rho(x)} &= \frac{\partial f}{\partial \rho} - \frac{d}{dx} \left( \frac{\partial f}{\partial \rho^{(1)}} \right) + \frac{d^2}{dx^2} \left( \frac{\partial f}{\partial \rho^{(2)}} \right) - \dots + (-1)^n \frac{d^n}{dx^n} \left( \frac{\partial f}{\partial \rho^{(n)}} \right). \tag{1.43}
\end{aligned}$$

Minima search. The minimum of a function,  $f(\vec{r})$ , implies that

$$\frac{\partial f}{\partial r_i} = 0 \quad \forall i. \tag{1.44}$$

The minimum of a functional,  $F[\rho]$ , implies that

$$\frac{\delta F}{\delta \rho(\vec{r})} = 0 \quad \forall \vec{r}. \tag{1.45}$$

We can also do constrained minimizations by using Lagrange multipliers. A typical example in DFT is the minimization of  $E[\rho]$  subject to the constraint

$$\int \rho(\vec{r}) d\vec{r} = N. \tag{1.46}$$

Thus we need to take the derivative of

$$\begin{aligned}
L[\rho] &= E_v[\rho] - \mu \left( \int \rho(\vec{r}) d\vec{r} - N \right) \\
0 &= \frac{\delta L}{\delta \rho(\vec{r})} = \frac{\delta E_v}{\delta \rho(\vec{r})} - \mu \\
&\Rightarrow \\
\frac{\delta E_v}{\delta \rho(\vec{r})} &= \mu, \tag{1.47}
\end{aligned}$$

a constant independent of  $\vec{r}$ ! But

$$\begin{aligned}
E_{N+\epsilon} - E_N &= E_v[\rho_{N+\epsilon}] - E_v[\rho_N] \\
&= \int \frac{\delta E_v}{\delta \rho(\vec{r})} (\rho_{N+\epsilon}(\vec{r}) - \rho_N(\vec{r})) d\vec{r} \\
&= \mu \int (\rho_{N+\epsilon}(\vec{r}) - \rho_N(\vec{r})) d\vec{r} \\
&= \mu \epsilon \\
&\Rightarrow \\
\mu &= \frac{\partial E_N}{\partial N}, \tag{1.48}
\end{aligned}$$

the ‘‘chemical potential.’’

### C. Thomas-Fermi-Dirac

$$\begin{aligned}
\mu &= \frac{\delta E_{\text{TFD}}}{\delta \rho(\vec{r})} \\
&= \frac{5}{3} c_{\text{TF}} \rho^{2/3}(\vec{r}) - \frac{4}{3} c_x \rho^{1/3}(\vec{r}) + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \tag{1.49}
\end{aligned}$$

If

$$v_{\text{ext}}(\vec{r}) \xrightarrow{r \rightarrow \infty} 0, \tag{1.50}$$

then we have that

$$\rho(\vec{r}) \xrightarrow{r \rightarrow \infty} 0. \tag{1.51}$$

So it suffices to solve the equation,

$$\frac{5}{3} c_{\text{TF}} \rho^{2/3}(\vec{r}) - \frac{4}{3} c_x \rho^{1/3}(\vec{r}) + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = 0. \tag{1.52}$$

Unfortunately we have

Teller’s Theorem (corrected and generalized by Balazs). In Thomas-Fermi and Thomas-Fermi-Dirac, no molecular system is stable against dissociation.

### D. Kohn-Sham Theory

The reason that molecules are not bound in Thomas-Fermi theory is that the kinetic energy is not well-enough approximated. So let us introduce some auxiliary orthonormal functions (called ‘‘orbitals’’) and write the total energy as

$$E = \sum_{i=1,N} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho], \tag{1.53}$$

where

$$\rho(\vec{r}) = \sum_{i,N} |\psi_i(\vec{r})|^2. \tag{1.54}$$

Minimization subject to the constraint

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j} \tag{1.55}$$

leads to

$$\begin{aligned}
 L &= E - \sum \epsilon_i \left( \int |\psi_i(\vec{r})|^2 d\vec{r} - 1 \right) \\
 0 &= \frac{\delta L}{\delta \psi_i^*(\vec{r})} \\
 &= \left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{r_{12}} d\vec{r}' + \frac{\delta E_{xc}}{\delta \rho(\vec{r})} - \epsilon_i \right] \psi_i(\vec{r})
 \end{aligned} \tag{1.56}$$

Thus to

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{r_{12}} d\vec{r}' + \frac{\delta E_{xc}}{\delta \rho(\vec{r})} \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \tag{1.57}$$

where

$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \tag{1.58}$$

is the exchange-correlation potential.

Notice that

$$T_s = \sum_{i=1,N} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle \tag{1.59}$$

is not the real kinetic energy. Part of  $E_{xc}$  is  $T - T_s$ .

The Kohn-Sham equation looks like the Hartree-Fock equation and has a similar solution. But there are two important differences:

- Hartree-Fock is always an approximation, but Kohn-Sham theory is exact when  $E_{xc}[\rho]$  is exact.
- $v_{xc}$  is a multiplicative operator, hence simpler than the Hartree-Fock exchange operator ( $\hat{K}$ ), which is an integral operator.

## E. Local Density Approximation (LDA)

Spectroscopic Constants of Diatomic Molecules Calculated with the LDA <sup>a</sup>						
molécule	$r_e$ (bohr)		$D_e$ (eV)		$\omega_e$ (cm <sup>-1</sup> )	
	Exp	LDA	Exp	LDA	Exp	LDA
H <sub>2</sub>	1,40	1,45	4,8	4,9	4 400	4 190
Li <sub>2</sub>	5,05	5,12	1,1	1,0	350	330
B <sub>2</sub>	3,00	3,03	3,0	3,9	1 050	1 030
C <sub>2</sub>	2,35	2,35	6,3	7,3	1 860	1 880
N <sub>2</sub>	2,07	2,07	9,9	11,6	2 360	2 380
O <sub>2</sub>	2,28	2,27	5,2	7,6	1 580	1 620
F <sub>2</sub>	2,68	2,61	1,7	3,4	890	1 060
Na <sub>2</sub>	5,82	5,67	0,8	0,9	160	160
Al <sub>2</sub>	4,66	4,64	1,8	2,0	350	350
Si <sub>2</sub>	4,24	4,29	3,1	4,0	510	490
P <sub>2</sub>	3,58	3,57	5,1	6,2	780	780
S <sub>2</sub>	3,57	3,57	4,4	5,9	730	720
Cl <sub>2</sub>	3,76	3,74	2,5	3,6	560	570

<sup>a</sup> Table taken from the reference: A.D. Becke, J. Chem. Phys. **84**, 4524 (1986).  
Observations on the performance of the LDA

- not bad for optimizing geometries
- a disaster for bond energies
- not bad for vibrational frequencies

## Recommended Literature

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## 1.2 TDDFT

The formal basis for modern time-dependent density-functional theory (TDDFT) is an article by Runge and Gross [9]. It was not the first article to propose a formalism for TDDFT and the theorems presented were not completely correct in their initial formulation. But the formalism presented by Runge and Gross is particularly elegant and any difficulties have been corrected by other researchers in the field. This is a normal process for any new formalism. A notable example is that the initial proofs of the Hohenberg-Kohn theorems also had hidden problems which are now much better understood and corrected.

### I. Some Preliminaries

The time-dependent behavior of an  $N$ -electron system is described by the time-dependent Schrödinger equation,

$$\hat{H}(t)\Psi(1, 2, \dots, N, t) = i\hbar \frac{\partial \Psi(1, 2, \dots, N, t)}{\partial t}. \quad (1.60)$$

The expectation value of an observable,  $\hat{O}$ , is

$$\langle \hat{O} \rangle(t) = \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle. \quad (1.61)$$

It follows that,

$$i\hbar \frac{\partial \langle \hat{O} \rangle}{\partial t}(t) = i\hbar \left\langle \frac{\partial \Psi(t)}{\partial t} \right| \hat{O}(t) | \Psi(t) \rangle + i\hbar \langle \Psi(t) | \hat{O}(t) \left| \frac{\partial \Psi(t)}{\partial t} \right\rangle + i\hbar \langle \Psi(t) | \frac{\partial \hat{O}}{\partial t}(t) | \Psi(t) \rangle$$

$$\begin{aligned}
&= -\langle \Psi(t) | \hat{H}(t) \hat{O}(t) | \Psi(t) \rangle + \langle \langle \Psi(t) | \hat{O}(t) \hat{H}(t) | \Psi(t) \rangle \rangle + i\hbar \langle \Psi(t) | \frac{\partial \hat{O}}{\partial t}(t) | \Psi(t) \rangle \\
&= \langle \Psi(t) | [\hat{O}(t), \hat{H}(t)] | \Psi(t) \rangle + i\hbar \langle \Psi(t) | \frac{\partial \hat{O}}{\partial t}(t) | \Psi(t) \rangle.
\end{aligned} \tag{1.62}$$

We want to recast these equations in the context of DFT. Our hamiltonian has the form,

$$\hat{H}(t) = -\frac{\hbar}{2m_e} \sum_i \nabla_i^2 + \sum_i \hat{v}_{ext}(i, t) + \sum_{i<j} \frac{e^2}{r_{i,j}}, \tag{1.63}$$

where the notation

$$i = (x_i, y_i, z_i, \sigma_i). \tag{1.64}$$

has been introduced. Notice that the external potential acts locally by simple multiplication. It thus represents an, in general time-dependent, electric field. This constraint is necessary if one wishes to take advantage of the Hohenberg-Kohn theorems in the static limit. Magnetic fields are not included which is worrisome when one realizes that any time-dependent electric field is necessarily associated with a magnetic field, but there are generalizations of DFT and TDDFT to treat electromagnetic fields. These later generalizations will not be treated here, in the interest of simplicity and because magnetic effects are really not very important for the problems we will treat.

Our objective is to replace  $\Psi(1, 2, \dots, N, t)$  with a quantity, such as the charge density,

$$\rho(1, t) = N \int \int \dots \int \Psi(1, 2, \dots, N, t) \Psi^*(1, 2, \dots, N, t) d2d3 \dots dN. \tag{1.65}$$

which only depends on the coordinates of a single electron. That this can be done is not *a priori* obvious because we can easily imagine that the instantaneous charge must at least be supplemented by some information about how the charge flows. In fact, formal TDDFT is ultimately based upon the current density,

$$\begin{aligned}
\mathbf{j}(1, t) &= \frac{N\hbar}{i2m_e} \int \int \dots \int [(\nabla_1 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) - \text{c.c.}] d2d3 \dots dN \\
&= \frac{N\hbar}{m_e} \Im m \left[ \int \int \dots \int (\nabla_1 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) d2d3 \dots dN \right].
\end{aligned} \tag{1.66}$$

In the particular cas of a Slater determinant,

$$\Psi(t) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1, t) & \psi_2(1, t) & \dots & \psi_N(1, t) \\ \psi_1(2, t) & \psi_2(2, t) & \dots & \psi_N(2, t) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N, t) & \psi_2(N, t) & \dots & \psi_N(N, t) \end{vmatrix}, \tag{1.67}$$

then

$$\mathbf{j}(1, t) = \frac{\hbar}{2m_e} \sum_{i=1, N} \{[\nabla \psi_i(1, t)] \psi_i^*(1, t) - \text{c.c.}\}. \tag{1.68}$$

The current density satisfies the famous continuity equation,

$$\frac{\partial \rho(1, t)}{\partial t} + \nabla \cdot \mathbf{j}(1, t) = 0. \tag{1.69}$$

This is a very physical equation. By using the divergence theorem, we can write for a volume  $V$  with surface  $S$ ,

$$\begin{aligned} \frac{\partial}{\partial t} \int_V \rho(\mathbf{r}\sigma, t) d\mathbf{r} &= - \int_V \nabla \cdot \mathbf{j}(\mathbf{r}\sigma, t) dv \\ &= - \int_S \mathbf{j}(\mathbf{r}\sigma, t) \cdot \mathbf{n}(\mathbf{r}) ds, \end{aligned} \quad (1.70)$$

where  $\mathbf{n}$  is the unit vector normal to the surface. The very physical interpretation is that the variation of the charge in the volume  $V$  is equal to minus the integral of the flux of current across the surface.

Proof of the Continuity Equation.

$$\begin{aligned} \frac{\partial \rho(1, t)}{\partial t} &= N \int \int \cdots \int \left[ \left( \frac{\partial}{\partial t} \Psi(1, 2, \dots, N, t) \right) \Psi^*(1, 2, \dots, N, t) + \text{c.c.} \right] d2d3 \cdots dN \\ &= \frac{N}{i\hbar} \int \int \cdots \int \left[ (\hat{H}(t) \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) - \text{c.c.} \right] d2d3 \cdots dN \\ &= \frac{-N\hbar}{i2m_e} \int \int \cdots \int \left[ \left( \sum_i \nabla_i^2 \Psi(1, 2, \dots, N, t) \right) \Psi^*(1, 2, \dots, N, t) - \text{c.c.} \right] d2d3 \cdots dN \\ &= \frac{-N\hbar}{i2m_e} \int \int \cdots \int \left[ (\nabla_1^2 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) - \text{c.c.} \right] d2d3 \cdots dN \\ &= \frac{-N\hbar}{i2m_e} \nabla_1 \cdot \left\{ \int \int \cdots \int [(\nabla_1 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) - \text{c.c.}] d2d3 \cdots dN \right\} \\ &= -\nabla_1 \cdot \mathbf{j}(1, t), \end{aligned} \quad (1.71)$$

Notice that we have made an integration by parts with  $i \neq 1$ ,

$$\int (\nabla_i^2 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) di = - \int (\nabla_i \Psi(1, 2, \dots, N, t)) \cdot (\nabla_i \Psi^*(1, 2, \dots, N, t)) di \quad (1.72)$$

in passing from the 3rd to the 4th line. Thus,

$$\int [(\nabla_i^2 \Psi(1, 2, \dots, N, t)) \Psi^*(1, 2, \dots, N, t) - \text{c.c.}] di = 0. \quad (1.73)$$

♡

Nous can also write the current as an expectation value,

$$\mathbf{j}(1, t) = \langle \Psi(t) | \hat{\mathbf{j}} | \Psi(t) \rangle, \quad (1.74)$$

where

$$\hat{\mathbf{j}}(\mathbf{r}\sigma, t) = \frac{\hbar}{2m_e i} \sum_{i=1, N} (\nabla_i \delta(\mathbf{x} - \mathbf{x}_i) + \delta(\mathbf{x} - \mathbf{x}_i) \nabla_i). \quad (1.75)$$

Thus,

$$\begin{aligned} \mathbf{j}(1, t) &= \langle \Psi(t) | \hat{\mathbf{j}} | \Psi(t) \rangle \\ &= \frac{\hbar}{2m_e i} \sum_{i=1, N} \langle \Psi(t) | (\nabla_i \delta(\mathbf{x} - \mathbf{x}_i) + \delta(\mathbf{x} - \mathbf{x}_i) \nabla_i) | \Psi(t) \rangle \\ &= \frac{\hbar}{2m_e i} \sum_{i=1, N} (-\langle \nabla_i \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_i) | \Psi(t) \rangle + \langle \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_i) | \nabla_i \Psi(t) \rangle) \\ &= \frac{N\hbar}{2m_e i} (\langle \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) | \nabla_1 \Psi(t) \rangle - \langle \nabla_1 \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) | \Psi(t) \rangle), \end{aligned} \quad (1.76)$$

in agreement with Eq. (1.66). As the operator  $\hat{\mathbf{j}}$  is independent of time, the equation of motion is,

$$i\hbar \frac{\partial \langle \hat{\mathbf{j}} \rangle}{\partial t}(t) = \langle \Psi(t) | [\hat{\mathbf{j}}, \hat{H}(t)] | \Psi(t) \rangle, \quad (1.77)$$

## II. First Runge-Gross Theorem

At time  $t_0$ , the state of our  $N$ -electron system is described by a wave function  $\Psi_0$ .

Theorem. If  $v_{ext}$  can be expressed as a Taylor series in time, then  $v_{ext}$  is determined up to an additive function of time by the time-dependent density.

Remark.

$$\begin{aligned} v_{ext}(1, t) &= \sum_{k=0}^{\infty} c_k(1) (t - t_0)^k \\ c_k(1) &= \frac{1}{k!} \frac{\partial^k}{\partial t^k} v_{ext}(1, t) |_{t=t_0}. \end{aligned} \quad (1.78)$$

Most reasonable potentials satisfy this criterion or at least approach it arbitrarily well.

Corollary. The wave function is a bifunctional of the time-dependent density and of the wave function at time  $t_0$  up to an arbitrary phase factor,

$$\Psi(t) = \Psi[\rho, \Psi_0](t) e^{i\phi(t)}. \quad (1.79)$$

If our system is in its ground state at time  $t_0$  then we can remove the dependence on  $\Psi_0$  to obtain,

$$\Psi(t) = \Psi[\rho](t) e^{i\phi(t)}. \quad (1.80)$$

Proof of the Corollary.

$$\begin{aligned} \rho(\mathbf{r}t) &\Rightarrow N, v_{ext}(\mathbf{r}, t) + C(t) \\ &\Rightarrow \hat{H}(t) + C(t) \\ &\Rightarrow \Psi(t) = \Psi[\rho, \Psi_0](t) e^{i \int_{t_0}^t C(t') dt'}. \end{aligned} \quad (1.81)$$

If our system is in its ground state at time  $t_0$ , the first Hohenberg-Kohn theorem tells us that  $\Psi_0$  is a functional of  $\rho$ . We can thus eliminate  $\Psi_0$  as an independent variable in the functional  $\Psi$ .

♡

In order to prove the theorem we need to show that two potentials differing by more than a function of time will necessarily lead to two different densities. The proof of the theorem involves a lemma concerning the current density,

Lemma. If  $v_{ext}(1, t) - v'_{ext}(1, t) \neq c(t)$ , then  $\mathbf{j}(t) \neq \mathbf{j}'(t)$ .

Remark. This is the same thing as  $\mathbf{j}(t) = \mathbf{j}'(t) \Rightarrow v_{ext}(1, t) - v'_{ext}(1, t) = c(t)$ .



Proof of the Lemma The equation of motion for the current is,

$$\begin{aligned}
i \frac{\partial}{\partial t} [\mathbf{j}(1, t) - \mathbf{j}(1', t)] &= \langle \Psi(t) | [\hat{\mathbf{j}}, \hat{H}(t) - \hat{H}'(t)] | \Psi(t) \rangle \\
&= \langle \Psi(t) | [\hat{\mathbf{j}}, v_{ext}(t) - v'_{ext}(t)] | \Psi(t) \rangle \\
&= \langle \Psi(t) | \hat{\mathbf{j}} (v_{ext}(t) - v'_{ext}(t)) | \Psi(t) \rangle - \langle \Psi(t) | (v_{ext}(t) - v'_{ext}(t)) \hat{\mathbf{j}} | \Psi(t) \rangle \\
&= \frac{N}{2i} \langle \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) \nabla_1 (v_{ext}(t) - v'_{ext}(t)) | \Psi \rangle \\
&\quad - \frac{N}{2i} \langle \nabla_1 \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) (v_{ext}(t) - v'_{ext}(t)) | \Psi \rangle \\
&\quad - \frac{N}{2i} \langle \Psi(t) | (v_{ext}(t) - v'_{ext}(t)) \delta(\mathbf{x} - \mathbf{x}_1) | \Psi(t) \rangle \\
&\quad + \frac{N}{2i} \langle \nabla_1 (v_{ext}(t) - v'_{ext}(t)) \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) | \Psi(t) \rangle \\
&= \frac{N}{2i} \langle \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) [\nabla_1 (v_{ext}(t) - v'_{ext}(t))] | \Psi \rangle \\
&\quad + \frac{N}{2i} \langle \Psi(t) | [\nabla_1 (v_{ext}(t) - v'_{ext}(t))] \delta(\mathbf{x} - \mathbf{x}_1) | \Psi(t) \rangle \\
&= \frac{N}{i} \langle \Psi(t) | \delta(\mathbf{x} - \mathbf{x}_1) [\nabla_1 (v_{ext}(t) - v'_{ext}(t))] | \Psi \rangle \\
&= \frac{N}{i} \rho(\mathbf{x}, t) [\nabla_1 (v_{ext}(t) - v'_{ext}(t))] . \tag{1.82}
\end{aligned}$$

As  $v_{ext}(1, t) - v'_{ext}(1, t) \neq c(t)$ , and the external potentials can be developed in Taylor series,

$$v_{ext}(1, t) - v'_{ext}(1, t) = \sum_{k=0}^{\infty} u_k(1) (t - t_0)^k, \tag{1.83}$$

there is a first  $k$  for which  $u_k(1) \neq 0$ . For this value of  $k$ ,

$$i \frac{\partial^{k+1}}{\partial t^{k+1}} [\mathbf{j}(1, t) - \mathbf{j}(1', t)] |_{t=t_0} = \frac{N}{i} \rho(\mathbf{x}, t) (\nabla_1 u_k(\mathbf{x}_1)). \tag{1.84}$$

It follows that,

$$\frac{\partial^{k+1}}{\partial t^{k+1}} [\mathbf{j}(1, t) - \mathbf{j}(1', t)] |_{t=t_0} \neq 0, \tag{1.85}$$

which means that if the two currents are the same at  $t = t_0$ , then the two currents will be different an instant later.

♡

We can finally do the

Proof of the Theorem We want to show that  $\mathbf{j}(1, t) \neq \mathbf{j}'(1, t) \Rightarrow \rho(1, t) \neq \rho'(1, t)$ . We will use the continuity equation,

$$\frac{\partial}{\partial t} (\rho(1, t) - \rho'(1, t)) = -\nabla \cdot (\mathbf{j}(1, t) - \mathbf{j}'(1, t)) \tag{1.86}$$

Once again, there is a first  $k$  for which  $u_k(1) \neq 0$ . For this value of  $k$ ,

$$\begin{aligned} \frac{\partial^{k+2}}{\partial t^{k+2}} (\rho(1, t) - \rho'(1, t)) |_{t=t_0} &= -\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}} (\mathbf{j}(1, t) - \mathbf{j}'(1, t)) |_{t=t_0} \\ &= -\nabla \cdot [\rho(1, t_0) \nabla u_k(\mathbf{x}_1)]. \end{aligned} \quad (1.87)$$

We have that  $\rho(1, t) \neq \rho'(1, t)$  provided we can show that  $\nabla \cdot [\rho(1, t_0) \nabla u_k(\mathbf{x}_1)] \neq 0$ . In order to do this we will suppose that  $\nabla \cdot [\rho(1, t_0) \nabla u_k(\mathbf{x}_1)] = 0$  for  $u_k \neq \text{const.}$  and we will seek a contradiction. Consider the following multidimensional integration by parts,

$$\begin{aligned} \int \rho(1, t_0) [\nabla u_k(1)]^2 d1 &= \int_S \rho(1, t_0) u_k(1) \nabla u_k(1) \cdot d\mathbf{s} \\ &\quad - \int u_k(1) \nabla \cdot [\rho(1, t_0) \nabla u_k(1)] d1. \end{aligned} \quad (1.88)$$

The second integral on the right hand side is zero by assumption. The first integral on the right is zero on condition that  $u_k(\mathbf{r}\sigma) \rightarrow 0$  fast enough. It is always zero for a finite system. It follows that the left hand side integral is zero and that the integrand (which is always non negative) is zero which finishes the proof of the theorem.

♡

### III. Formulation Kohn-Sham

Thanks to the first Runge-Gross theorem we have that the external potential of the real system is a functional of the density. It is also true for the fictitious noninteracting system. It follows that we can write the time-dependent Kohn-Sham equation,

$$\left[ -\frac{1}{2} \nabla^2 + v_{ext}(1, t) + \int \frac{\rho(2, t)}{r_{12}} d2 + v_{xc}[\rho](1, t) \right] \psi_i(1, t) = i\hbar \frac{\partial \psi_i(1, t)}{\partial t}. \quad (1.89)$$

For some people, this is a sufficient argument. We do not need to express the TDDFT exchange-correlation potential as a functional derivative of anything at all. On the otherhand, the exchange-correlation potential has to be approximated somehow. A first approximation supposes that the xc potential reacts instantaneously and without memory to any temporal change in the charge density. This is called the adiabatic approximation and allows us to write

$$v_{xc}[\rho](1, t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(1)}, \quad (1.90)$$

where  $\rho_t(1)$  is  $\rho(1, t)$  evaluated at fixed  $t$ . The adiabatic approximation is local in time.

### IV. Second Runge-Gross Theorem

This subject is complicated and so we will just outline some of the main issues. One way to attack time-dependent problems in Quantum Chemistry is by using the Dirac-Frenkel variational principle. This means finding the stationary points of the action,

$$A = \int_{t_0}^{t_1} \langle \Psi(t') | i \frac{\partial}{\partial t'} - \hat{H}(t') | \Psi(t') \rangle dt'. \quad (1.91)$$

Runge and Gross proposed that this action, which is also a functional of  $\rho$  according to the first theorem, may also serve as a basis for TDDFT.

Now it is true that the exact wave function is an extremum,

$$0 = i \frac{\partial \Psi(t)}{\partial t} - \hat{H}(t) \Psi(t), \quad (1.92)$$

but we can also find other extrema for less general types of wave functionals, such as over the set of Slater determinants. In traditional Quantum Chemistry, this is one of the advantages of the Dirac-Frenkel variational principle. But it is a weakness if you want to develop an exact formalism. In particular, the constraint that the density be  $v$ -representable limits the range of possible variations with the unexpected result that  $A = 0$  has other solutions besides the exact  $\rho(t)$ .

Robert van Leeuwen [10] showed how to get around these problems by replacing the Dirac-Frenkel action by the Keldysh action,

$$\tilde{A}[v_{ext}] = i \ln \text{Tr} \left[ e^{\beta \mu \hat{N}} \hat{U}(-i\beta, 0) \right], \quad (1.93)$$

where the time-evolution operator,  $U(t, t')$ , is defined on the Keldysh contour shown in Fig. 1.1. On the Keldysh contour,

$$\frac{\delta \tilde{A}}{\delta v_{ext}(1, t)} = \rho(1, t). \quad (1.94)$$

A Legendre transformation,

$$A[\rho] = -\tilde{A}[v_{ext}] + \int \rho(1) v_{ext}(1) d1, \quad (1.95)$$

leads to

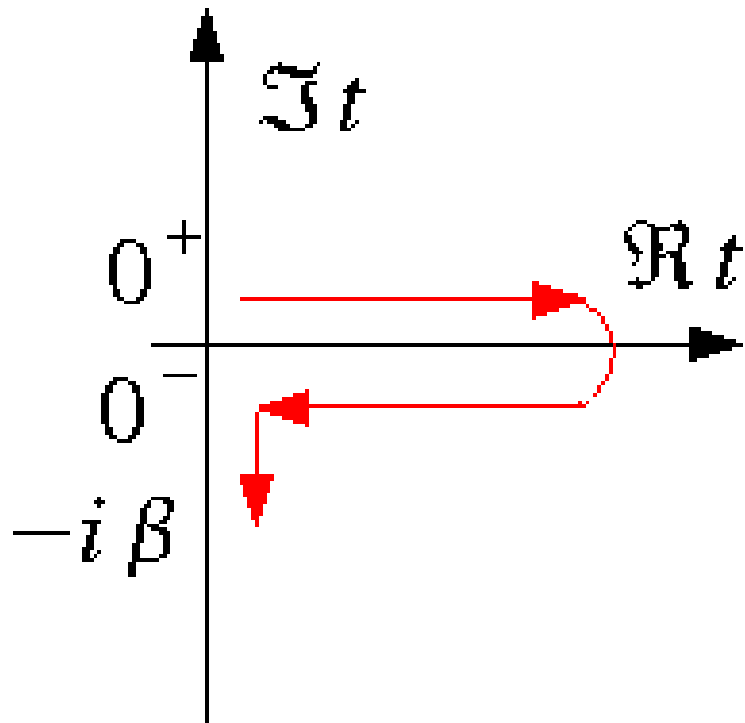
$$v_{ext}(1t) = \frac{\partial A}{\partial \rho(1t)}. \quad (1.96)$$

also on the Keldysh contour. aussi sur le contour de Keldysh.

As these techniques also apply to the noninteracting system, we can conclude that  $v_{xc}(1, t)$  and its derivatives are well-defined in terms of derivatives of a Keldysh action. By studying the properties of this exchange-correlation action, we can hope for a better understanding of exchange-correlation approximations beyond the adiabatic approximation in TDDFT.

### Recommended Literature

- R. van Leeuwen, Int. J. Mod. Phys. B **15**, 1969 (2001). “Key concepts in time-dependent density-functional theory”
- E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984). “Density functional theory for time-dependent systems”



## Keldysh contour

Figure 1.1: The Keldysh contour.

# Chapter 2

## Linear Response Theory

In optical physics, linear response (LR) theory relates the response of a molecular property (for example, the dynamic polarizability) to the excited states of the unperturbed molecule (or more exactly to the absorption spectrum in the case of the dynamic polarizability). Our emphasis in this chapter will be on this aspect of LR theory. We will assume that the Schrödinger equation has already been solved for the unperturbed molecule and we will seek a description of the properties of the molecule subject to a time-dependent perturbation in terms of the exact solutions of the unperturbed system.

In the chapters following this one, we will carry out the inverse operation. Instead of seeking information regarding the response of the molecule in terms of a knowledge of its excited states, we will seek information about the excited states beginning from a knowledge of the time-dependent response properties of the molecule. This will eventually allow us to extract from density-functional theory (DFT) information about excited states without referring to the wave functions for either the ground or excited states of the molecule.

### 2.1 Dynamic Polarizability

Consider a time-dependent perturbation applied to a molecule initially in its ground stationary state. We would like to express the response of a property to this perturbation in terms of the states of the unperturbed system. An important example is shown in Fig. 2.1. This example will be treated at the end of this section. On the other hand, it would be an error to specialize too quickly because LR theory is sufficiently general that it may also be applied to problems as diverse as NMR chemical shifts and circular dichroism spectra. For this reason, we will keep the treatment general and gradually specialize as needed.

We assume that the exact solution is known for the Schrödinger equation for the unperturbed system (molecule.) The time-independent equation is,

$$\hat{H}\Psi_I = E_I\Psi_I. \quad (2.1)$$

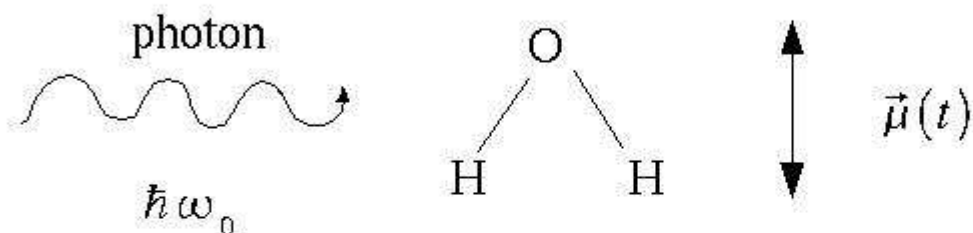
The corresponding time-dependent equation is,

$$\hat{H}\Psi_I(t) = i\hbar\frac{\partial}{\partial t}\Psi_I(t), \quad (2.2)$$

with,

$$\Psi_I(t) = \Psi_I e^{-iE_I t/\hbar}. \quad (2.3)$$

## Polarisation Électronique



- Modèle classique d'un photon

$$\vec{\varepsilon}(t) = \vec{\varepsilon} \cos \omega_0 t$$

$$v(\vec{r}, t) = e \vec{\varepsilon}(t) \cdot \vec{r}$$

- Moment dipolaire induit

$$\delta \vec{\mu}(t) = -e (\langle \Psi_0 | \vec{r} | \delta \Psi_0(t) \rangle + \langle \delta \Psi_0(t) | \vec{r} | \Psi_0 \rangle)$$

Figure 2.1: A water molecule perturbed by a photon. The photon is modeled by a classical time-dependent electric field. We are interested in the induced dipole moment which is also a function of time.

Careful! The notation is compact:  $\Psi_I(t) \neq \Psi_I$ .

Now apply the time-dependent perturbation,  $\hat{b}(t)$ . The equation governing the time evolution of the perturbed system is,

$$\left(\hat{H} + b(t)\right) \Psi_0(t) = i\hbar \frac{\partial}{\partial t} \Psi_0(t). \quad (2.4)$$

Without loss of generality,

$$\Psi_0(t) = (\Psi_0 + \delta\Psi_0(t) + \dots) e^{-iE_0 t/\hbar}, \quad (2.5)$$

which allows us to deduce that the linear response of the ground state,  $\delta\Psi_0(t)$ , satisfies,

$$\hat{b}(t)\Psi_0 = \left(i\hbar \frac{\partial}{\partial t} - \hat{H} + E_0\right) \delta\Psi_0(t). \quad (2.6)$$

Note the phase factor in Eq. (2.5). It is there to guarantee that the usual expression from Rayleigh-Schrödinger perturbation theory is recovered in the static limit.

We will solve this equation using Fourier transformations (Appendix 2.2). First we must rewrite Eq. (2.6) as,

$$i\hbar \delta\Psi_0(t) = \int_{-\infty}^t \left[\hat{b}(t')\Psi_0 + (\hat{H} - E_0) \delta\Psi_0(t')\right] dt'. \quad (2.7)$$

This form is still general. If the perturbation is only applied beginning at some finite time, it is only necessary that  $\hat{b}(t)$  be defined as zero at all times prior to applying the perturbation. Nevertheless the cases which interest us the most are those for which the perturbation is applied adiabatically (that is, gradually) beginning from time  $t = -\infty$  so that transient effects have time to die out and the system response has time to stabilize.

The form (2.7) is not yet ideal for carrying out Fourier transforms. The form,

$$i\hbar \delta\Psi_0(t) = \int_{-\infty}^{+\infty} \theta(t - t') \left[\hat{b}(t')\Psi_0 + (\hat{H} - E_0) \delta\Psi_0(t')\right] dt', \quad (2.8)$$

is better. Here  $\theta$  is the Heaviside (or “step”) function,

$$\theta(t) = \begin{cases} 1 & ; t > 0 \\ 0 & ; t < 0 \end{cases} \quad (2.9)$$

In fact, very soon we will replace  $\theta$  by

$$\theta_\eta(t) = \begin{cases} e^{+\eta t} & ; t > 0 \\ 0 & ; t < 0 \end{cases} \quad (2.10)$$

which contains a convergence factor with an infinitesimal,  $\eta > 0$ , which guarantees that  $\delta\Psi(t = -\infty) = 0$ . We can then apply the Fourier transformation convolution theorem (Appendix 2.2) to obtain,

$$i\hbar \delta\Psi_0(\omega) = \theta(\omega) \left[\hat{b}(\omega)\Psi_0 + (\hat{H} - E_0) \delta\Psi_0(\omega)\right], \quad (2.11)$$

but what is the Fourier transformation of the Heaviside function? It is here that we make use of the convergence factor to assure that the Fourier transformation is well-defined:

$$\begin{aligned} \theta(\omega) &= \int_{-\infty}^{+\infty} e^{+i\omega t} \theta(t) dt \\ &= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^{+\infty} e^{+i\omega t} \theta_\eta(t) dt \end{aligned}$$

$$\begin{aligned}
&= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^{+\infty} e^{i(\omega+i\eta)t} \theta(t) dt \\
&= \lim_{\eta \rightarrow 0^+} \int_0^{+\infty} e^{i(\omega+i\eta)t} dt \\
&= \lim_{\eta \rightarrow 0^+} \left[ \frac{e^{i(\omega+i\eta)t}}{i(\omega+i\eta)} \right]_0^{+\infty} \\
&= \lim_{\eta \rightarrow 0^+} \frac{+i}{\omega+i\eta} \\
&= \frac{+i}{\omega}.
\end{aligned} \tag{2.12}$$

Equation (2.11) becomes,

$$i\hbar \delta\Psi_0(\omega) = \frac{+i}{\omega} \left[ \hat{b}(\omega)\Psi_0 + (\hat{H} - E_0) \delta\Psi_0(\omega) \right], \tag{2.13}$$

or,

$$\left[ E_0 - \hat{H} + \hbar\omega \right] \delta\Psi_0(\omega) = \hat{b}(\omega)\Psi_0. \tag{2.14}$$

Equation (2.14) is now in the usual form for applying Rayleigh-Schrödinger perturbation theory. We will assume intermediate normalisation,

$$\langle \delta\Psi_0(\omega) | \Psi_0 \rangle = 0, \tag{2.15}$$

and then deduce,

$$\delta\Psi_0(\omega) = \sum_{I \neq 0} \Psi_I \frac{\langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle}{\hbar(\omega - \omega_I)}, \tag{2.16}$$

where,

$$\omega_I = E_I - E_0, \tag{2.17}$$

is the  $I$ th excitation energy of the unperturbed system.

**Exercise:** Explicitly carryout the intermediate steps between Eq. (2.14) and the solution (2.16).

In order to go further, we assume that the perturbation is monochromatic,

$$\begin{aligned}
\hat{b}(t) &= b \cos(\omega_0 t) \\
&= b \frac{e^{+i\omega_0 t} + e^{-i\omega_0 t}}{2} \\
\hat{b}(\omega) &= \frac{b}{2} \left[ \int_{-\infty}^{+\infty} e^{+i(\omega+\omega_0)t} dt + \int_{-\infty}^{+\infty} e^{+i(\omega-\omega_0)t} dt \right] \\
&= \pi b [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)].
\end{aligned} \tag{2.18}$$

Then

$$\begin{aligned}
\delta\Psi_0(\omega) &= \sum_{I \neq 0} \Psi_I \frac{\langle \Psi_I | \pi \hat{b} [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)] | \Psi_0 \rangle}{\hbar(\omega - \omega_I)} \\
&= \sum_{I \neq 0} \Psi_I \langle \Psi_I | \hat{b} | \Psi_0 \rangle \frac{\pi}{\hbar} \left[ \frac{\delta(\omega + \omega_0)}{-\omega_0 - \omega_I} + \frac{\delta(\omega - \omega_0)}{\omega_0 - \omega_I} \right] \\
&= \sum_{I \neq 0} \Psi_I \langle \Psi_I | \hat{b} | \Psi_0 \rangle \frac{\pi}{\hbar} \left\{ \frac{\omega_I [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)]}{\omega_0^2 - \omega_I^2} - \frac{\omega_0 [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)]}{\omega_0^2 - \omega_I^2} \right\}
\end{aligned} \tag{2.19}$$



As,

$$\begin{aligned}
\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \pi [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)] d\omega &= \frac{e^{+i\omega t} - e^{-i\omega t}}{2} \\
&= i \sin(\omega_0 t) \\
\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \pi [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)] d\omega &= \frac{e^{+i\omega t} + e^{-i\omega t}}{2} \\
&= \cos(\omega_0 t), \tag{2.20}
\end{aligned}$$

then,

$$\begin{aligned}
\delta\Psi_0(t) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \delta\Psi_0(\omega) d\omega \\
&= \left[ \sum_{I \neq 0} \Psi_I \frac{\omega_I \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \right] \cos(\omega_0 t) - i \left[ \sum_{I \neq 0} \Psi_I \frac{\omega_0 \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \right] \sin(\omega_0 t). \tag{2.21}
\end{aligned}$$

The linear response,  $\delta\langle \hat{a} \rangle$ , of an observable,  $a$ , is given by,

$$\begin{aligned}
\delta\langle \hat{a} \rangle(t) &= \langle \Psi_0 | \hat{a} | \delta\Psi_0(t) \rangle + \langle \delta\Psi_0(t) | \hat{a} | \Psi_0 \rangle \\
&= \sum_{I \neq 0} \frac{\omega_I \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \cos(\omega_0 t) - i \sum_{I \neq 0} \frac{\omega_0 \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \sin(\omega_0 t) \\
&+ \sum_{I \neq 0} \frac{\omega_I \langle \Psi_0 | \hat{b} | \Psi_I \rangle \langle \Psi_I | \hat{a} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \cos(\omega_0 t) + i \sum_{I \neq 0} \frac{\omega_0 \langle \Psi_0 | \hat{b} | \Psi_I \rangle \langle \Psi_I | \hat{a} | \Psi_0 \rangle}{\hbar(\omega_0^2 - \omega_I^2)} \sin(\omega_0 t) \\
&= \left[ \sum_{I \neq 0} \frac{2\omega_I \Re(\langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle)}{\hbar(\omega_0^2 - \omega_I^2)} \right] \cos(\omega_0 t) \\
&+ \left[ \sum_{I \neq 0} \frac{2\omega_0 \Im(\langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle)}{\hbar(\omega_0^2 - \omega_I^2)} \right] \sin(\omega_0 t). \tag{2.22}
\end{aligned}$$

This result is very powerful. We see that the response to a perturbation at frequency  $\omega_0$  is at the same frequency. The phase is also the same if the operators  $\hat{a}$  and  $\hat{b}$  are both real (polarizability) or both imaginary (NMR). The phase is  $\pi/2$  if one of  $\hat{a}$  and  $\hat{b}$  is real and the other is imaginary (circular dichroism.)

We finally arrive at the point where we will specialize to the case of the electric polarizability. This is defined in terms of the response of the molecular dipole moment to an applied electric field. The dipole moment of a molecule is the sum of an electronic contribution and a nuclear contribution,

$$\mu_{r_j} = -e \langle \Psi_0 | r_j | \Psi_0 \rangle + e \sum_A Z_A R_{jA}; \quad r_j = x, y, z. \tag{2.23}$$

Note that the dipole moment is defined here so as to point from the negative end of the molecule towards the positive end. It can be shown that the dipole moment is well defined, in the sense of being independent of the choice of origin, provided that the molecule is neutral. We will apply an electric field of the form,

$$\mathcal{E}_{r_j}(t) = \mathcal{E}_{r_j} \cos(\omega t); \quad r_j = x, y, z. \tag{2.24}$$

The corresponding perturbation is,

$$\begin{aligned}
\hat{b}(t) &= +e \mathcal{E} \cdot \mathbf{r} \cos(\omega t) \\
\hat{b} &= +e \mathcal{E} \cdot \mathbf{r}. \tag{2.25}
\end{aligned}$$

The dynamic polarizability is the proportionality tensor between the linear response of the dipole moment and the applied field,

$$\mu_{r_i}(t) = \mu_{r_i} + \sum_{r_j=x,y,z} \alpha_{r_i,r_j}(\omega) \mathcal{E}_{r_j} \cos(\omega t) + \cdots ; r_i = x, y, z. \quad (2.26)$$

The polarizability is fundamental for describing the interaction of light with matter. It enters into the theory of refractive indices and dielectric constants. It also enters into modeling intermolecular forces and into the theory of solvated molecules. For us, the dynamic polarizability will be a way to access excited states.

At optical frequencies, the variation in the electric field is too rapid for the nuclei to follow, so we may consider them clamped in place. The response of the dipole moment is then entirely electronic and we may write,

$$\begin{aligned} \delta\mu_{r_i}(t) &= -e\langle\Psi_0|r_i|\delta\Psi_0(t)\rangle - e\langle\delta\Psi_0(t)|r_i|\Psi_0\rangle \\ &= -e^2 \sum_{r_j=x,y,z} \left[ \sum_{I\neq 0} \frac{2\omega_I \Re(\langle\Psi_0|r_i|\Psi_I\rangle\langle\Psi_I|r_j|\Psi_0\rangle)}{\hbar(\omega^2 - \omega_I^2)} \right] \mathcal{E}_{r_j} \cos(\omega t). \end{aligned} \quad (2.27)$$

By definition, then, the dynamic polarizability is,

$$\begin{aligned} \alpha_{r_i,r_j}(\omega) &= \sum_{I\neq 0} \frac{2e^2\omega_I \Re(\langle\Psi_0|r_i|\Psi_I\rangle\langle\Psi_I|r_j|\Psi_0\rangle)}{\hbar(\omega_I^2 - \omega^2)} \\ &= \sum_{I\neq 0} \frac{e^2 f_I^{r_i,r_j}}{m_e(\omega_I^2 - \omega^2)}, \end{aligned} \quad (2.28)$$

where evidently,

$$f_I^{r_i,r_j} = \frac{2m_e\omega_I}{\hbar} \Re(\langle\Psi_0|r_i|\Psi_I\rangle\langle\Psi_I|r_j|\Psi_0\rangle). \quad (2.29)$$

As we often do not know the orientation of the molecules, it is the average dynamic polarizability,

$$\begin{aligned} \alpha(\omega) &= \frac{1}{3} \sum_{r_i=x,y,z} \alpha_{r_i,r_i}(\omega) \\ &= \sum_{I\neq 0} \frac{e^2 f_I}{m_e(\omega_I^2 - \omega^2)}, \end{aligned} \quad (2.30)$$

which is important (Fig. 2.2). The oscillator strength is defined by the expression,

$$\begin{aligned} f_I &= \frac{1}{3} (f_I^{x,x} + f_I^{y,y} + f_I^{z,z}) \\ &= \frac{2m_e\omega_I}{3\hbar} (|\langle\Psi_0|x|\Psi_I\rangle|^2 + |\langle\Psi_0|y|\Psi_I\rangle|^2 + |\langle\Psi_0|z|\Psi_I\rangle|^2), \end{aligned} \quad (2.31)$$

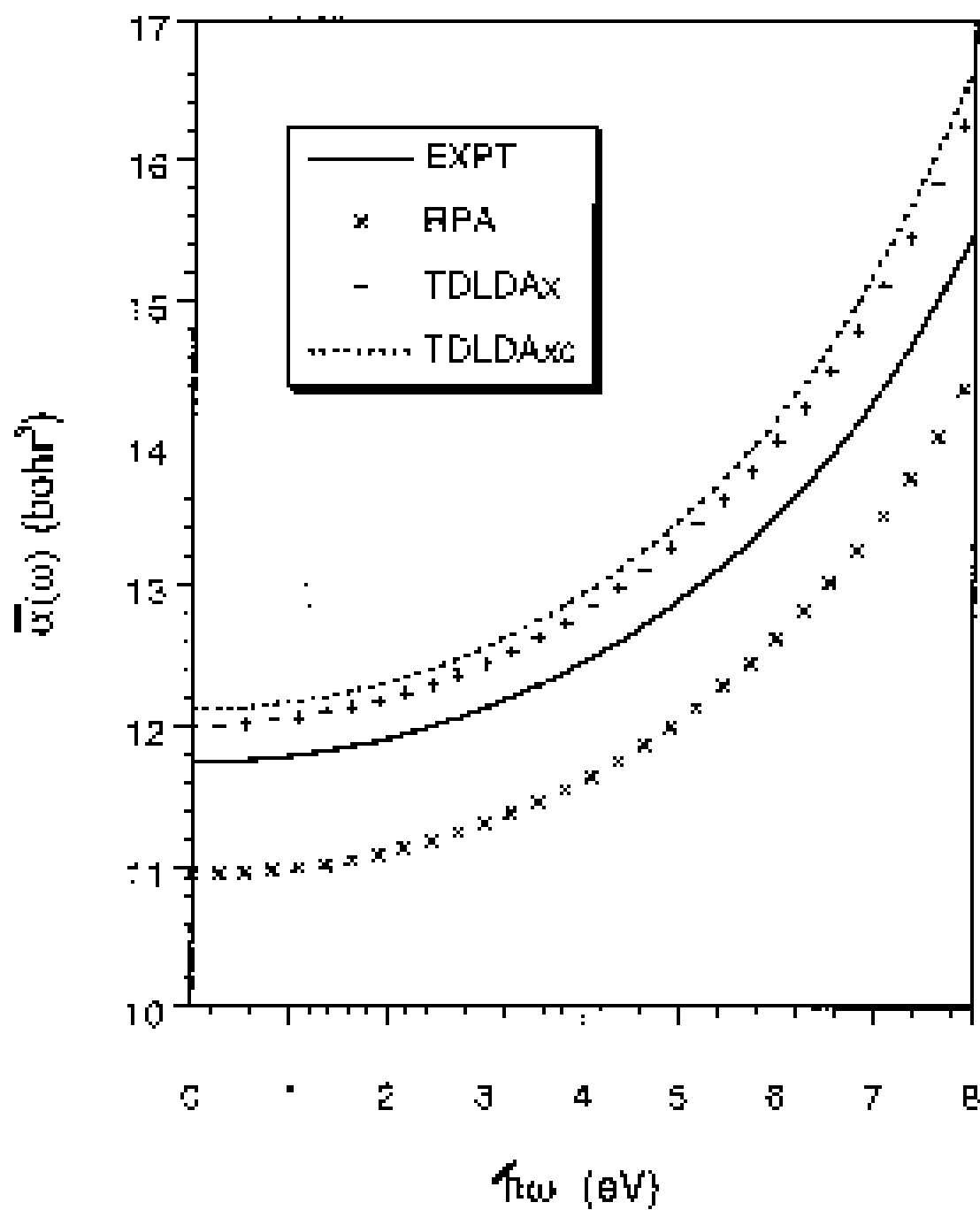
is a pure number (without units) which is related to peak intensity in absorption spectra as will be discussed in more detail in the following section.

## 2.2 Absorption Spectra

The result,

$$\alpha(\omega) = \sum_{I\neq 0} \frac{e^2 f_I}{m_e(\omega_I^2 - \omega^2)}, \quad (2.32)$$

## DYNAMIC MEAN POLARIZABILITY

Figure 2.2: Dynamic polarizability of the molecule N<sub>2</sub>[11].

is the very important sum-over-states (SOS) theorem (SOS is not just *Save Our Ship* ;-). The main objective of this section is to show that not only are excitation energies accessible from absorption spectra, but oscillator strengths are too. Thus the importance of the SOS theorem is that the dynamic polarizability can be expressed in terms of information contained in UV absorption spectra.

The absorbance,  $A$ , of a sample is given by the ratio of the incident intensity,  $I_0$ , to that leaving the sample,  $I$ ,

$$\begin{aligned} A &= -\frac{1}{\ln(10)} \left( \frac{I}{I_0} \right) \\ &= -\frac{1}{\ln(10)} \ln \left( \frac{I}{I_0} \right) \\ I &= I_0 e^{-A \ln(10)}. \end{aligned} \quad (2.33)$$

According to Beer's law, for a dilute thin sample with thickness  $\ell$  and concentration  $C$ ,

$$A = \epsilon C \ell, \quad (2.34)$$

where  $\epsilon$  is the absorption coefficient and is characteristic of the molecules whose spectrum is being measured. The absorbed intensity is,

$$\begin{aligned} I_{abs} &= I - I_0 \\ &= I_0 \left( 1 - e^{-A \ln(10)} \right) \\ &= I_0 \left( 1 - e^{-\epsilon_A C \ell \ln(10)} \right) \\ &= I_0 \epsilon C \ln(10) \ell + \dots \end{aligned} \quad (2.35)$$

Hence the absorption coefficient is,

$$\epsilon = \frac{I_{abs}}{\ell} \frac{1}{C I_0 \ln(10)}. \quad (2.36)$$

For an electromagnetic wave, the intensity is given by the magnitude of the Poynting vector,

$$I_0 = \frac{c \mathcal{E}^2}{8\pi} \text{ or in SI units: } \frac{c \epsilon_0 \mathcal{E}^2}{2}. \quad (2.37)$$

As the absorbed intensity is the energy absorbed per time per light beam cross section area, the quantity

$$\frac{I_{abs}}{\ell} = \frac{P_{abs}}{V}, \quad (2.38)$$

is the power (that is the energy per time) absorbed per volume of sample illuminated. Also

$$\frac{P_{abs}}{V} = N_A C p_{abs}, \quad (2.39)$$

where  $p_{abs}$  is the power absorbed per molecule. Putting it all together, we have

$$\epsilon = \frac{8\pi N_A}{c \mathcal{E}^2 \ln(10)} p_{abs}. \quad (2.40)$$

Thus we have succeeded in expressing the absorption coefficient in terms of a typical molecular quantity,  $p_{abs}$ .

It remains to analyze  $p_{abs}$ . To do this, we will use Fermi's (second) golden rule (see for example, Ref. [12] pp. 282-285). We will continue to use time-dependent adiabatic perturbation theory as developed in the previous section, but this time it is important to take into account that the perturbation is very quick (the photon is absorbed rapidly.) The perturbation is applied at time  $t - \Delta t$  and is finished at time  $t$ . The transition probability is given through linear order by the square of,

$$\begin{aligned} a_I(t) &= \langle \Psi_I e^{-iE_I t/\hbar} | \Psi_0(t) \rangle \\ &= \langle \Psi_I e^{-iE_I t/\hbar} | \delta \Psi_0(t) e^{-iE_0 t/\hbar} \rangle \\ &= \langle \Psi_I | \delta \Psi_0(t) \rangle e^{+i\omega_I t}. \end{aligned} \quad (2.41)$$

Its derivative is,

$$\begin{aligned} i\hbar \frac{\partial a_I(t)}{\partial t} &= \langle \Psi_I | i\hbar \frac{\partial \delta \Psi_0(t)}{\partial t} - \hbar \omega_I \delta \Psi_0(t) \rangle e^{+i\omega_I t} \\ &= \langle \Psi_I | i\hbar \frac{\partial \delta \Psi_0(t)}{\partial t} - (\hat{H} - E_0) \delta \Psi_0(t) \rangle e^{+i\omega_I t} \\ &= \langle \Psi_I | \hat{b}(t) | \Psi_0 \rangle e^{+i\omega_I t}, \end{aligned} \quad (2.42)$$

because of the relation,

$$\hat{b}(t) \Psi_0 = \left( i\hbar \frac{\partial}{\partial t} - \hat{H} + E_0 \right) \delta \Psi_0(t). \quad (2.43)$$

Thus,

$$a_I(t) = \frac{1}{i\hbar} \int_{t-\Delta t}^t \langle \Psi_I | \hat{b}(t') | \Psi_0 \rangle e^{+i\omega_I t'} dt'. \quad (2.44)$$

For deriving Fermi's golden rule we choose,

$$\hat{b}(t) = \hat{b} e^{-i\omega_0 t}, \quad (2.45)$$

The integral is,

$$\begin{aligned} a_I(t) &= \frac{1}{i\hbar} \langle \Psi_I | \hat{b} | \Psi_0 \rangle \int_{t-\Delta t}^t e^{-i(\omega_0 - \omega_I)t'} dt' \\ &= \frac{1}{i\hbar} \langle \Psi_I | \hat{b} | \Psi_0 \rangle \frac{e^{-i(\omega_0 - \omega_I)t} - e^{-i(\omega_0 - \omega_I)(t-\delta t)}}{i(\omega_0 - \omega_I)} \\ &= \langle \Psi_I | \hat{b} | \Psi_0 \rangle e^{-i(\omega_0 - \omega_I)t} \frac{1 - e^{+i(\omega_0 - \omega_I)\delta t}}{(-\hbar)(\omega_0 - \omega_I)} \\ &= 2 \langle \Psi_I | \hat{b} | \Psi_0 \rangle e^{-i(\omega_0 - \omega_I)t} e^{+i(\omega_0 - \omega_I)\delta t/2} \frac{i \sin((\omega_0 - \omega_I)\delta t/2)}{\hbar(\omega_0 - \omega_I)}. \end{aligned} \quad (2.46)$$

Then the transition probability is,

$$\begin{aligned} P(\omega_0; \delta t) &= |a_I(t)|^2 \\ &= \frac{4 |\langle \Psi_I | \hat{b} | \Psi_0 \rangle|^2 \sin^2((\omega_0 - \omega_I)\delta t/2)}{\hbar^2 (\omega_0 - \omega_I)^2}. \end{aligned} \quad (2.47)$$

The transition rate (probability of transition per time) is,

$$\begin{aligned} w_I(\omega) &= \frac{P(\omega; \delta t)}{\delta t} \\ &= \frac{2\pi}{\hbar^2} |\langle \Psi_I | \hat{b} | \Psi_0 \rangle|^2 \delta(\omega - \omega_I), \end{aligned} \quad (2.48)$$

because

$$\lim_{t \rightarrow +\infty} \frac{1}{t} \frac{\sin^2(\omega t/2)}{\omega^2} = \frac{\pi}{2} \delta(\omega). \quad (2.49)$$

Equation (2.48) is the Fermi's famous (second) golden rule. One often sees it in the form,

$$T_{i \rightarrow f} = \frac{2\pi}{\hbar} |H_{i,f}|^2 \rho(E), \quad (2.50)$$

where  $\rho(E)$  is the density of states. In the case of discrete energy levels,

$$\begin{aligned} \rho(E) &= \sum_I \delta(E - E_I) \\ &= \frac{1}{\hbar} \sum_I \delta(\omega - \omega_I), \end{aligned} \quad (2.51)$$

and we find the expression (??).

The power per molecule due to the transition  $\omega_I$  is,

$$\begin{aligned} p_{abs}(\omega) &= (\hbar\omega) w_I(\omega) \\ &= \frac{2\pi\omega_I |\langle \Psi_I | \hat{b} | \Psi_0 \rangle|^2}{2\hbar} \delta(\omega - \omega_I) \end{aligned} \quad (2.52)$$

Putting,

$$\hat{b} = e \mathcal{E} \cdot \mathbf{r} / 2, \quad (2.53)$$

and averaging over the three spacial directions, we find,

$$p_{abs} = \frac{\pi e^2 \mathcal{E}^2 f_I}{4m_e} \delta(\omega_0 - \omega_I). \quad (2.54)$$

The reason for the factor of 2 in Eq. (??) is so as to treat,

$$\begin{aligned} \hat{b}(t) &= \hat{b} \cos(\omega_0 t) \\ &= \hat{b} \frac{1}{2} (e^{+i\omega_0 t} + e^{-i\omega_0 t}), \end{aligned} \quad (2.55)$$

instead of the “half” given by Eq. (2.45). We can finally put this equation in the expression (2.40) to obtain,

$$\epsilon = \frac{2\pi^2 N_A e^2 f_I}{m_e c \ln(10)} \delta(\omega_0 - \omega_I). \quad (2.56)$$

This for a stick spectrum. In reality the peaks have a width and it is best to use,

$$\begin{aligned} f_I &= \frac{m_e c \ln(10)}{2\pi^2 N_A e^2} \int \epsilon(\omega) d\omega \\ &= \frac{m_e c \ln(10)}{\pi N_A e^2} \int \epsilon(\nu) d\nu. \end{aligned} \quad (2.57)$$

In SI units that is,

$$f_I = \frac{m_e c 4\pi \ln(10) \epsilon_0}{\pi N_A e^2} \int \epsilon(\nu) d\nu. \quad (2.58)$$

**Exercise:** Show that,

$$f_I = (1,44 \times 10^{-19} \text{ mol} \cdot \text{cm} \cdot \text{s} / \text{L}) \int \epsilon(\nu) d\nu. \quad (2.59)$$

Given the importance of oscillator strengths, it is good to look at some variations on the basic formula,

$$f_I^x = \frac{2\omega_I m_e}{\hbar} |\langle \Psi_0 | \hat{x} | \Psi_I \rangle|^2. \quad (2.60)$$

These formulae are based on the following observations:

$$\begin{aligned} \hat{p}_x &= -i\hbar \frac{\partial}{\partial x} \\ [\hat{x}, \hat{p}_x] &= +i\hbar \\ \langle \Psi_0 | [\hat{x}, \hat{p}_x] | \Psi_0 \rangle &= \sum_i^{elec} \langle \Psi_0 | [\hat{x}(i), \hat{p}(i)] | \Psi_0 \rangle \\ &= \sum_i^{elec} i\hbar \langle \Psi_0 | \Psi_0 \rangle \\ &= i\hbar N \\ [\hat{H}, \hat{x}] &= \frac{1}{2m_e} [\hat{p}_x^2, \hat{x}] \\ &= \frac{1}{2m_e} (\hat{p}_x [\hat{p}_x, \hat{x}] + [\hat{p}_x, \hat{x}] \hat{p}_x) \\ &= \frac{-i\hbar}{m_e} \hat{p}_x. \end{aligned} \quad (2.61)$$

Thus the length form [Eq. (2.61)] is equivalent to a velocity form,

$$\begin{aligned} f_I^x &= \frac{2\omega_I m_e}{\hbar} \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle \\ &= -\frac{2m_e}{\omega_I \hbar^3} \langle \Psi_0 | [\hat{H}, \hat{x}] | \Psi_I \rangle \langle \Psi_I | [\hat{H}, \hat{x}] | \Psi_0 \rangle \\ &= +\frac{2}{m_e \hbar \omega_I} |\langle \Psi_0 | \hat{p}_x | \Psi_I \rangle|^2. \end{aligned} \quad (2.62)$$

There is also a mixed form,

$$\begin{aligned} f_I^x &= \frac{2\omega_I m_e}{\hbar} \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle \\ &= \frac{2m_e}{\hbar^2} \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | [\hat{H}, \hat{x}] | \Psi_0 \rangle \\ &= -\frac{2im_e}{\hbar} \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{p}_x | \Psi_0 \rangle. \end{aligned} \quad (2.63)$$

We can also prove the Thomas-Reiche-Kuhn (TRK) sum rule,

$$\begin{aligned} N &= -\frac{i}{\hbar} \langle \Psi_0 | [\hat{x}, \hat{p}_x] | \Psi_0 \rangle \\ &= -\frac{i}{\hbar} \sum_I (\langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{p}_x | \Psi_0 \rangle - \langle \Psi_0 | \hat{p}_x | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle) \end{aligned}$$

TABLE VIII. Comparison of TDLDAXC Cauchy coefficients (in a.u.) with those from other *ab initio* methods and with experiment.  $R_{\text{Nuc}}=2.074$  bohr.

Method	Basis set	$S_0$	$S_{-1}^2$	$S_{-4}$	$S_{-6}$
TD-DPRT Calculations					
TDLDAXC	TZVP+	11.48	11.92	32.71	114.5
	BK90	12.96	10.56	31.93	127.98
	Sadlej	10.44	12.11	34.83	131.3
	DSadlej	13.99	12.19	34.00	128.2
	88CGTO	14.04	11.55	29.32	99.12
	106CGTO	14.03	11.73	31.70	121.1
Experiment <sup>b</sup>					
14 <sup>c</sup>					
Other theory					
TDHP <sup>d</sup>	[11s8p4d1f]	13.96	11.56	27.60	100.51
TDHP <sup>e</sup>	[7s5p3d]		11.44	27.53	83.36
TDHP <sup>f</sup>	DSadlej	14.01	11.54	27.39	83.84
MCTDHP <sup>g</sup>	[11s8p4d1f]		11.06	25.61	68.53
MCTDHP <sup>h</sup>	[8s6p4d1f]			28.92	94.51
SOPPA <sup>i</sup>	DSadlej		11.42	29.24	98.6

<sup>a</sup>Mean static polarizability.

<sup>b</sup>Reference 66.

<sup>c</sup>Exact value equals number of electrons.

<sup>d</sup>Time-dependent Hartree-Pock calculation of Ref. 46.

<sup>e</sup>Time-dependent Hartree-Pock calculation of Ref. 67.

<sup>f</sup>Time-dependent Hartree-Pock calculation of Ref. 44

<sup>g</sup>Multiconfigurational time-dependent Hartree-Pock calculation of Ref. 46. Six orbital active space.

<sup>h</sup>Multiconfigurational time-dependent Hartree-Pock calculation of Ref. 60. Twelve orbital active space.

<sup>i</sup>Second-order polarization propagator approximation calculation of Ref. 44.

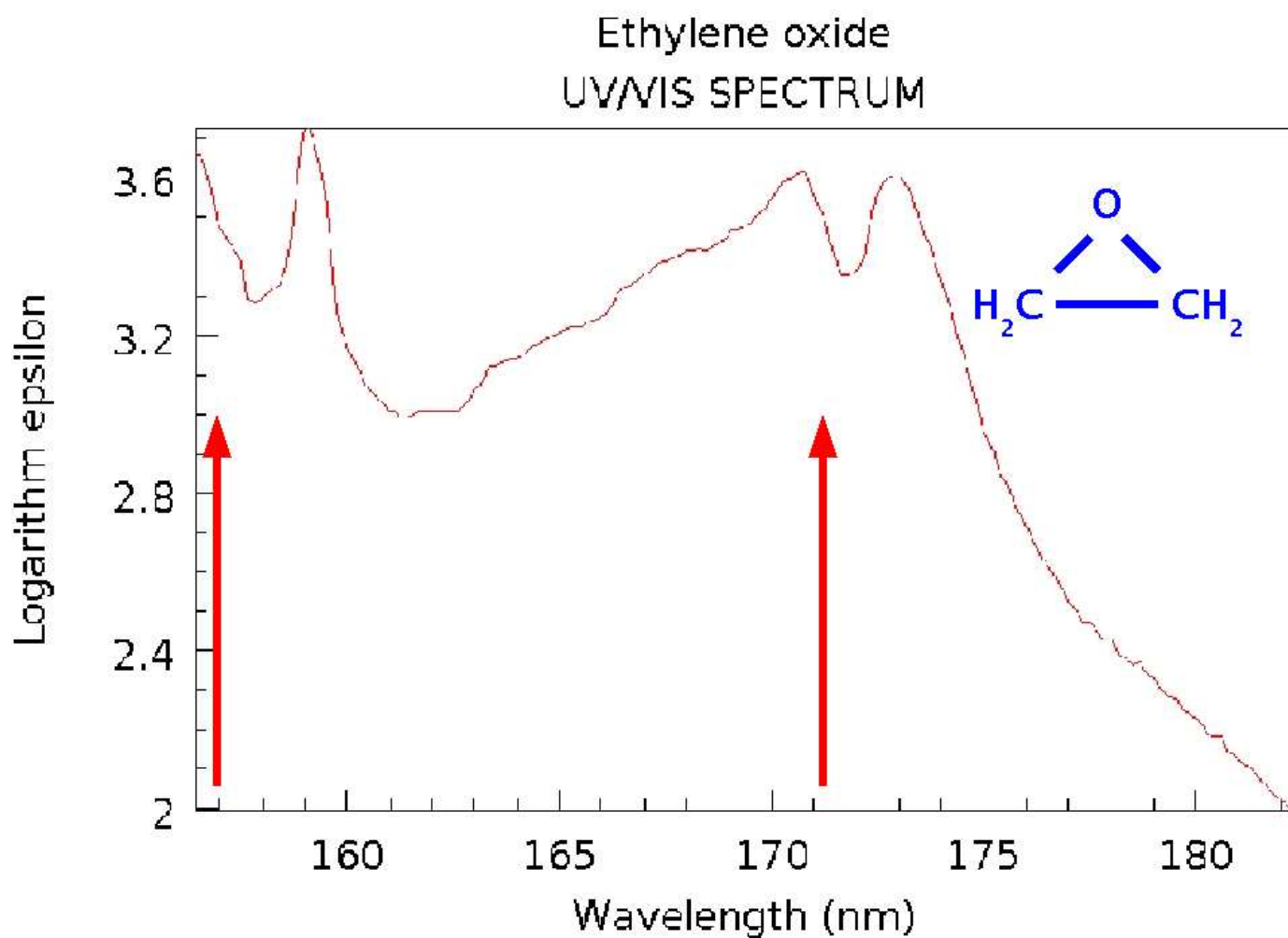
Figure 2.3: Performance of the TRK sum rule ( $S_0$ ) in a finite basis set for the 14-electron molecule  $\text{N}_2$  [11].

$$\begin{aligned}
&= \frac{m_e}{\hbar^2} \sum_I \left( \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | [\hat{H}, \hat{x}] | \Psi_0 \rangle - \langle \Psi_0 | [\hat{H}, \hat{x}] | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle \right) \\
&= \frac{m_e}{\hbar} \sum_I 2\omega_I \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle \\
&= \sum_I f_I^x.
\end{aligned} \tag{2.64}$$

Thus the sum of the oscillator strengths is the number of electrons. On the other hand, it is important to realize that the relations (2.61) and hence the equivalence of the different forms of the oscillator strength and the TRK sum rule are only true for operators and not for matrices expressed in a finite basis set. This is shown for TDDFT calculations in Fig. 2.3.

In reality, even gas phase spectra are complicated by vibrational effects. The spectrum of oxirane (Fig. 2.4) is a case in point. Not only are the electronic transitions not sticks since the peaks have width, but also the wide peaks have structure. This structure is probably partly due to the fact that this molecule undergoes photochemical ring opening. In any event the job of extracting oscillator strengths is certainly not a simple one since overlapping peaks have to be separated. This is one of the reasons that molecular oscillator strengths are only known approximately with few exceptions (Fig. 2.5).





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Figure 2.4: Gas phase UV spectrum for oxirane. Higher resolution measurements allow the extraction of the two electronic transitions shown in red. The width and structure in the two peaks is due to underlying vibrational structure.

TABLE VIII. Comparison of the TDLDA/LB94 and TDLDA/AC-LDA oscillator strengths with experiment and other theoretical values.

State	Oscillator strengths <sup>a</sup> [excitation energies (eV)]				
	TDLDA/LB94	TDLDA/AC-LDA	Expt. <sup>b</sup>	TDHP <sup>c</sup>	CI <sup>d</sup>
CO					
A <sup>1</sup> Π	0.136 [7.98]	0.136 [8.18]	0.1762 [~8.4]	0.1705 [8.89]	0.1668
N <sub>2</sub>					
b <sup>1</sup> Σ <sub>v</sub> <sup>+</sup>	0.399 [14.21]	0.420 [14.00]	0.278 [~14.2]	0.15 [15.03]	0.31
c <sup>1</sup> Σ <sub>v</sub> <sup>+</sup>	0.307 [13.46]	0.248 [12.87]	0.279 [~12.9]	0.65 [14.34]	0.26
Total <sup>1</sup> Σ <sub>v</sub> <sup>+</sup>	0.706	0.668	0.557	0.80	0.57
o <sup>1</sup> Π <sub>v</sub>	0.126 [13.96]	0.077 [13.42]	0.080 [~13.6]	...	0.15
c <sup>1</sup> Π <sub>v</sub>	0.148 [13.57]	0.417 [13.06]	0.145 [~13.2]	0.091 [13.91]	0.09
b <sup>1</sup> Π <sub>v</sub>	0.243 [12.90]	0.017 [13.00]	0.243 [~12.8]	0.32 [15.10]	0.41
Total <sup>1</sup> Π <sub>v</sub>	0.517	0.511	0.468	...	0.65
CH <sub>2</sub> O					
3 <sup>1</sup> A <sub>1</sub>	0.144 [9.62]	0.055 [9.38]	0.0238 [~9.0]	0.035 08 [9.54]	0.035 [10.3]
2 <sup>1</sup> A <sub>1</sub>	0.061 [8.64]	0.071 [7.57]	0.0281 [~8.0]	0.056 94 [8.32]	0.14 [8.90]
Total <sup>1</sup> A <sub>1</sub>	0.205	0.126	0.0519	0.092 02	0.175
3 <sup>1</sup> B <sub>2</sub>	0.043 [9.67]	0.044 [8.95]	0.0198 [~8.8]	0.020 41 [9.24]	0.81 [9.97]
2 <sup>1</sup> B <sub>2</sub>	0.011 [8.47]	0.018 [7.70]	0.0605 [~8.3]	0.038 21 [8.22]	0.15 [8.69]
1 <sup>1</sup> B <sub>2</sub>	0.070 [7.32]	0.055 [6.73]	0.0413 [~7.3]	0.022 79 [7.39]	0.060 [7.52]
Total <sup>1</sup> B <sub>2</sub>	0.124	0.117	0.1216	0.081 41	1.02

<sup>a</sup>Degeneracy weighted.

<sup>b</sup>Oscillator strengths from Refs. 82 and 84 (CO), Ref. 83 (N<sub>2</sub>), and Ref. 85 (CH<sub>2</sub>O). (The CO oscillator strength of Ref. 84 has been decreased by 2.5% in accordance with the recommendation on p. 69 of Ref. 82.) Rough experimental energies, estimated from the same references are also indicated.

<sup>c</sup>Time-dependent Hartree–Fock results for CO: from Table II (energy) and Table III (oscillator strength) of Ref. 104. TDHP results for N<sub>2</sub>: from Table 4 (energy) and Table 6 (oscillator strength) of Ref. 87. TDHP results for CH<sub>2</sub>O: From Table I of Ref. 111.

<sup>d</sup>Configuration interaction results for CO from Table III of Ref. 112. CI results for N<sub>2</sub> from Ref. 113. CI results for CH<sub>2</sub>O from Table III of Ref. 114.

Figure 2.5: Some accurately known molecular oscillator strengths [13].

# Chapter 3

## DFT and TDDFT by Analogy

Before density-functional theory (DFT), there was the Hartree-Fock (HF) approximation and the usual Kohn-Sham formulation of DFT looks a lot like HF even though they don't work exactly in the same fashion (normally DFT is more reliable.) Similarly before linear-response time-dependent density-functional theory (LR-TDDFT) there was linear-response time-dependent Hartree-Fock (LR-TDHF) which looks a lot like configuration interaction singles (CIS). We will take the historical approach here by doing HF, CIS, and LR-TDHF before DFT and TDDFT. This is one way to build some intuition about how TDDFT should work ... and also to prepare ourselves to be surprised when it doesn't work quite the way we think it should!

### 3.1 Second Quantization

Second quantization is a formalism which emphasizes operators and 1- and 2-electron matrix elements rather than Slater determinants. For us, it is an algebraic machine that we can use in developing computationally useful equations.

This section, with its "theorem-proof" style, is very mathematical. However I have reduced the size of the type for those details which I consider to be less important.

#### *Two Elegant Formalisms*

Dirac:

$$|\psi_{i_1}\psi_{i_2}\cdots\psi_{i_N}| \rightarrow |i_1i_2\dots i_N\rangle \quad (3.1)$$

Second Quantization:

$$\begin{aligned} \hat{H} &= \sum_{i=1,N} \hat{h}(i) + \frac{1}{2} \sum_{i,j=1,N} \hat{v}(i,j) \\ &\rightarrow \\ \hat{H} &= \sum_{ij} h_{i,j} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{4} \sum_{ijkl} v_{ij,kl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \end{aligned} \quad (3.2)$$

Sometimes it is said that any manipulation done with second quantization could also be done without this formalism. Thus the only reasons to use second quantization are its elegance and its frequent use in the literature. However this reasoning is not quite correct because the fact that  $N$  never appears in the fundamental equation for  $\hat{H}$  also means that systems with an unknown or variable number of electrons may be treated. Such problems frequently arise for solids.

## I. Creation and Annihilation Operators

The language of second quantization supposes a predetermined underlying one-electron (spin) orbital basis set,  $\{\psi_1, \psi_2, \psi_3, \dots\}$ . This basis set should be complete and orthonormal.

$$\langle i|j\rangle = \int \psi_i^* \psi_j d\tau = \delta_{i,j}. \quad (3.3)$$

It allows us to construct kets which correspond to Slater determinants:

$$\begin{aligned} &| \rangle \\ &|i\rangle \\ &|ij\rangle \\ &|ijk\rangle \\ &\vdots \\ &\text{etc.} \end{aligned} \quad (3.4)$$

The state  $| \rangle$  is special. It is the Slater determinant corresponding to zero electrons and is called the vacuum state.

Definition.  $\mathcal{H}_N$  is the (Hilbert) space of  $N$ -electron functions. We thus have

$$\begin{aligned} | \rangle &\in \mathcal{H}_0 \\ |i\rangle &\in \mathcal{H}_1 \\ |ij\rangle &\in \mathcal{H}_2 \\ |ijk\rangle &\in \mathcal{H}_3 \\ &\vdots \\ &\text{etc.} \end{aligned} \quad (3.5)$$

Definition. The creation operator is defined by

$$\hat{a}_l^\dagger |ij\dots\rangle = |lij\dots\rangle. \quad (3.6)$$

We thus have that

$$\hat{a}_l^\dagger : \mathcal{H}_N \rightarrow \mathcal{H}_{N+1}. \quad (3.7)$$

In fact we see that Slater determinants are not among the most fundamental building blocks of the formalism because we can always build them by applying creation operators to the vacuum state.

$$\begin{aligned} &| \rangle \\ &\hat{a}_i^\dagger | \rangle = |i\rangle \\ &\hat{a}_i^\dagger \hat{a}_j^\dagger | \rangle = \hat{a}_i^\dagger |j\rangle = |ij\rangle \\ &\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger | \rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger |k\rangle = \hat{a}_i^\dagger |jk\rangle = |ijk\rangle \\ &\dots \end{aligned} \quad (3.8)$$

Let us consider in more detail the properties of creation operators.

Definition The anticommutator

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}. \quad (3.9)$$

Theorem

$$\{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = 0. \quad (3.10)$$

Proof An operator is defined by its action.

$$\begin{aligned} \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} |kl\dots\rangle &= (\hat{a}_i^\dagger \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i^\dagger) |kl\dots\rangle \\ &= |ijkl\dots\rangle + |jikl\dots\rangle \\ &= |ijkl\dots\rangle - |jikl\dots\rangle \\ &= 0 \end{aligned} \quad (3.11)$$

♥

Definition The adjoint,  $\hat{a}_i$ , of the creation operator,  $\hat{a}_i^\dagger$ , is the corresponding annihilation operator.

Theorem

$$\{\hat{a}_i, \hat{a}_j\} = 0. \quad (3.12)$$

Proof

$$\begin{aligned} 0 &= \{\hat{a}_i, \hat{a}_j\}^\dagger \\ &= (\hat{a}_i \hat{a}_j)^\dagger + (\hat{a}_j \hat{a}_i)^\dagger \\ &= \hat{a}_j^\dagger \hat{a}_i^\dagger + \hat{a}_i^\dagger \hat{a}_j^\dagger \\ &= \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} \end{aligned} \quad (3.13)$$

♥

Let us take stock of the action of  $\hat{a}_i$ .

Let us look at a simple example,

$$\begin{aligned} \hat{a}_i^\dagger &: \mathcal{H}_N \rightarrow \mathcal{H}_{N+1} \\ \hat{a}_i &: \mathcal{H}_N \rightarrow \mathcal{H}_{N-1}. \end{aligned} \quad (3.14)$$

We have used the closure relation,

$$\hat{1} = \sum |j\rangle\langle j|. \quad (3.15)$$

Notice my tendency to use a pseudo-Einstein convention: In the absence of explicit indices on a sum sign, then it is understood that the sum is over repeated indices unless otherwise specified.

In order to continue, we need the identity,

$$\begin{aligned} \langle mn|ij\rangle &= \frac{1}{2} \int \int (\psi_m^*(1)\psi_n^*(2) - \psi_n^*(1)\psi_m^*(2))(\psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2)) d1d2 \\ &= \int \int \psi_m^*(1)\psi_n^*(2)(\psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2)) d1d2 \\ &= \left( \int \psi_m^*(1)\psi_i(1) d1 \right) \left( \int \psi_n^*(2)\psi_j(2) d2 \right) - \left( \int \psi_m^*(1)\psi_j(1) d1 \right) \left( \int \psi_n^*(2)\psi_i(2) d2 \right) \\ &= \langle m|i\rangle\langle n|j\rangle - \langle m|j\rangle\langle n|i\rangle \\ &= \delta_{m,i}\delta_{n,j} - \delta_{m,j}\delta_{n,i}. \end{aligned} \quad (3.16)$$

Then

$$\begin{aligned} \hat{a}_i |mn\rangle &= \sum |j\rangle\langle j|\hat{a}_i |mn\rangle \\ &= \sum |j\rangle\langle mn|\hat{a}_i^\dagger|j\rangle^* \\ &= \sum |j\rangle\langle mn|ij\rangle^* \\ &= \sum |j\rangle\langle ij|mn\rangle \\ &= \sum |j\rangle(\delta_{m,i}\delta_{n,j} - \delta_{m,j}\delta_{n,i}) \\ &= \delta_{m,i}|n\rangle - \delta_{n,i}|m\rangle \\ &= \begin{cases} |n\rangle; & i = m \\ -|m\rangle; & i = n \\ 0; & \text{autrement} \end{cases} \end{aligned} \quad (3.17)$$

In general we have the

Theorème

$$\hat{a}_i |kl\dots\rangle = 0 \text{ si } i \notin \{k, l, \dots\}, \quad (3.18)$$

$$\hat{a}_i |kl\dots i\dots\rangle = (-1)^t |kl\dots \not{i}\dots\rangle, \quad (3.19)$$

where  $t$  is the number of transpositions needed to create the determinant  $|ikl\dots\rangle$ .

Corollary

$$\hat{a}_i^\dagger \hat{a}_i |kl\dots\rangle = n_i |kl\dots\rangle, \quad (3.20)$$

where

$$n_i = \begin{cases} 0; & i \notin \{k, l, \dots\} \\ 1; & i \in \{k, l, \dots\} \end{cases}. \quad (3.21)$$

Definition

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i \quad (3.22)$$

is the number operator for orbital  $i$ .

Theoreme

$$\{\hat{a}_i, \hat{a}_j^\dagger\} = \delta_{i,j} \quad (3.23)$$

Proof Consider

$$\{\hat{a}_i, \hat{a}_j^\dagger\} |kl\dots\rangle = (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |kl\dots\rangle \quad (3.24)$$

There are two cases, depending upon whether  $i$  is in  $\{kl\dots\}$  or not.

*Case 1* :  $i \notin \{kl\dots\}$ . Then

$$\begin{aligned} (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |kl\dots\rangle &= \hat{a}_i |jkl\dots\rangle \\ &= \delta_{i,j} |kl\dots\rangle. \end{aligned} \quad (3.25)$$

*case 2* :  $i \in \{kl\dots\}$ . Then

$$\begin{aligned} (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |kl\dots i\dots\rangle &= \hat{a}_i |jkl\dots i\dots\rangle + (-1)^t \hat{a}_j^\dagger |jkl\dots \not{i}\dots\rangle \\ &= (1 - \delta_{i,j}) \hat{a}_i |jkl\dots i\dots\rangle + (-1)^t \hat{a}_j^\dagger |kl\dots \not{i}\dots\rangle \\ &= (1 - \delta_{i,j}) (-1)^{t+1} |jkl\dots \not{i}\dots\rangle + (-1)^t |jkl\dots \not{i}\dots\rangle \\ &= \delta_{i,j} (-1)^t |jkl\dots \not{i}\dots\rangle \\ &= \delta_{i,j} |jkl\dots i\dots\rangle. \end{aligned} \quad (3.26)$$

♡

Lazy Notation

$$\begin{aligned} i &= \hat{a}_i \\ i^\dagger &= \hat{a}_i^\dagger. \end{aligned} \quad (3.27)$$

This notation is handy for long algebraic manipulations, but may lead to confusion. Nevertheless this lazy notation is more and more used in the literature. Our anticommutation relations may be summarized in this notation as

$$\begin{aligned} \{i, j\} &= \{i^\dagger, j^\dagger\} = 0 \\ \{i, j^\dagger\} &= \delta_{i,j}. \end{aligned} \quad (3.28)$$

## II. Second-Quantized Operators

We can make use of the work done up to now to write the Condon-Slater rules in the form,  
Theorem

$$\begin{aligned}\hat{H} &= \sum \langle i|\hat{h}|j\rangle i^\dagger j + \frac{1}{4} \sum \langle ij||kl\rangle i^\dagger j^\dagger lk \\ &= \sum \langle i|\hat{h}|j\rangle i^\dagger j + \frac{1}{2} \sum (ik||jl) i^\dagger j^\dagger lk.\end{aligned}\quad (3.29)$$

Reminder

$$\begin{aligned}\langle ij|\hat{v}|kl\rangle &= \langle ij||kl\rangle \\ &= (ik||jl) - (il||jk) \text{ (Notation de Mullikan).}\end{aligned}\quad (3.30)$$

More concretely,

$$\begin{aligned}(ij||kl) &= (ij|f_H|kl) \\ &= \int \int \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_k^*(\mathbf{x}_2)\psi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2,\end{aligned}\quad (3.31)$$

where,

$$\begin{aligned}f_H(\mathbf{x}_1, \mathbf{x}_2) &= f_H^{\sigma,\tau}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{1}{r_{12}},\end{aligned}\quad (3.32)$$

is the Hartree kernel. Thus

$$\begin{aligned}\sum \langle ij||kl\rangle i^\dagger j^\dagger lk &= \sum (ik||jl) i^\dagger j^\dagger lk - \sum (il||jk) i^\dagger j^\dagger lk \\ &= \sum (ik||jl) i^\dagger j^\dagger lk + \sum (il||jk) i^\dagger j^\dagger kl \\ &= \sum (ik||jl) i^\dagger j^\dagger lk + \sum (ik||jl) i^\dagger j^\dagger lk \\ &= 2 \sum (ik||jl) i^\dagger j^\dagger lk.\end{aligned}\quad (3.33)$$

Proof of the theorem It suffices to show that we obtain the same expressions for the matrix elements in the basis of Slater determinants that we have already obtained explicitly. For example: Given

$$|I\rangle = |i_1 i_2 \dots i_N\rangle. \quad (3.34)$$

Then

$$\begin{aligned}\langle I|\hat{h}|I\rangle &= \langle I| \left( \sum \langle i|\hat{h}|j\rangle i^\dagger j \right) |I\rangle \\ &= \sum \langle i|\hat{h}|j\rangle \langle I|i^\dagger j|I\rangle.\end{aligned}\quad (3.35)$$

Evidently

$$\langle I|i^\dagger j|I\rangle = 0 \quad (3.36)$$

except if  $i, j \in \{i_1, i_2, \dots, i_N\}$ . Now

$$i^\dagger j = \delta_{i,j} - j i^\dagger. \quad (3.37)$$

So

$$\begin{aligned}\langle I|\hat{h}|I\rangle &= \sum_{i,j \in I} \langle i|\hat{h}|j\rangle \left( \underbrace{\delta_{i,j}}_1 \langle I|I\rangle - \underbrace{\langle I|j i^\dagger|I\rangle}_0 \right) \\ &= \sum_{i \in I} \langle i|\hat{h}|i\rangle,\end{aligned}\quad (3.38)$$

which is the same result given by the Slater-Condon rules. Etc. etc. ♡

*Density Matrices*

Corollary Given

$$\begin{aligned}\hat{A}^{(1)} &= \sum_{i=1,N} \hat{a}^{(1)}(i) \\ \hat{A}^{(2)} &= \sum_{\substack{(i<j) \\ i,j=1,N}} \hat{a}^{(2)}(ij).\end{aligned}\tag{3.39}$$

Then the expectation values for the state  $|\Psi\rangle$  are given by

$$\begin{aligned}\langle \hat{A}^{(1)} \rangle &= \sum \langle i | \hat{a}^{(1)} | j \rangle \gamma_{j,i} \\ &= \text{tr } \mathbf{a}^{(1)} \gamma \\ \langle \hat{A}^{(2)} \rangle &= \frac{1}{4} \sum \langle ij | \hat{a}^{(2)} | kl \rangle \Gamma_{kl,ij} \\ &= \sum_{(i<j,k<l)} \langle ij | \hat{a}^{(2)} | kl \rangle \Gamma_{kl,ij} \\ &= \text{tr } \mathbf{a}^{(2)} \Gamma,\end{aligned}\tag{3.40}$$

where

$$\gamma_{j,i} = \langle \Psi | i^\dagger j | \Psi \rangle\tag{3.41}$$

is the 1-electron density matrix and

$$\Gamma_{kl,ij} = \langle \Psi | i^\dagger j^\dagger lk | \Psi \rangle\tag{3.42}$$

is the 2-electron density matrix.

Theorem

$$\begin{aligned}\text{tr } \gamma &= N \\ \text{tr } \Gamma &= N(N-1).\end{aligned}\tag{3.43}$$

Proof

$$\begin{aligned}\text{tr } \gamma &= \sum \gamma_{i,i} \\ &= \sum \langle i^\dagger i \rangle \\ &= \sum \langle \hat{n}_i \rangle \\ &= \langle \hat{n} \rangle \\ &= N,\end{aligned}\tag{3.44}$$

where

$$\hat{n} = \sum \hat{n}_i\tag{3.45}$$

is the number operator.

$$\begin{aligned}\text{tr } \Gamma &= \sum \Gamma_{ij,ij} \\ &= \sum \langle i^\dagger j^\dagger ji \rangle \\ &= -\sum \langle j^\dagger i^\dagger ji \rangle \\ &= -\sum \delta_{i,j} \langle j^\dagger i \rangle + \sum \langle j^\dagger ji^\dagger i \rangle \\ &= \sum \langle j^\dagger ji^\dagger i \rangle - \sum \langle i^\dagger i \rangle \\ &= \sum \langle \hat{n}_j \hat{n}_i \rangle - \sum \langle \hat{n}_i \rangle \\ &= \langle \hat{n} (\hat{n} - 1) \rangle \\ &= N(N-1).\end{aligned}\tag{3.46}$$

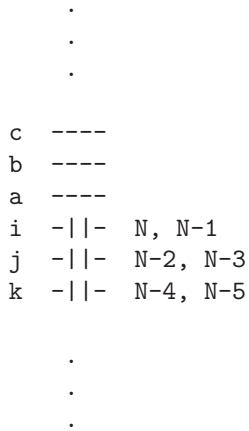


♡

### III. The Particle-Hole Representation

Consider a “change of coordinate” defined with respect to a Slater determinant,

$$|\Phi\rangle = |123\dots N\rangle. \tag{3.47}$$



We will introduce a new

Index Convention

$$\underbrace{abc\dots gh}_{\text{orbitales vides}} \quad | \quad \underbrace{ijklmn}_{\text{orbitales occupées}} \quad | \quad \underbrace{opq\dots xyz}_{\text{orbitales non spécifiées}} \tag{3.48}$$

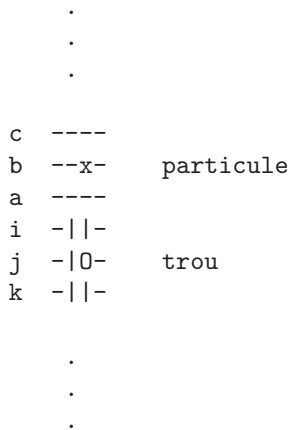
The operators

$$\hat{c}_i^\dagger = \hat{a}_i \tag{3.49}$$

“create holes” and the operators

$$\hat{c}_a^\dagger = \hat{a}_a^\dagger \tag{3.50}$$

“create particles” in the “vacuum state”  $|\Phi\rangle$ .



As

$$\begin{aligned} \{\hat{c}_r, \hat{c}_s\} &= \{\hat{c}_r^\dagger, \hat{c}_s^\dagger\} = 0 \\ \{\hat{c}_r, \hat{c}_s^\dagger\} &= \delta_{i,j}, \end{aligned} \tag{3.51}$$

we recover all the algebra of second quantization except that the form of the hamiltonian becomes more complicated.

**Definition** A second quantized operator is said to be *normally ordered* when all the annihilation operators are to the right of all the creation operators.

**Theoreme**

$$\begin{aligned}
\hat{H} - \langle \hat{H} \rangle &= \sum F_{a,b} \hat{c}_a^\dagger \hat{c}_b - \sum F_{i,j} \hat{c}_j^\dagger \hat{c}_i + \sum F_{i,b} \hat{c}_i \hat{c}_b + \sum F_{a,j} \hat{c}_a^\dagger \hat{c}_j^\dagger \\
&= \frac{1}{2} \sum (ab||cd) \hat{c}_a^\dagger \hat{c}_c^\dagger \hat{c}_d \hat{c}_b + \frac{1}{2} \sum (ij||kl) \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_i \hat{c}_k \\
&+ \sum (ab||kl) \hat{c}_a^\dagger \hat{c}_k^\dagger \hat{c}_b \hat{c}_l - \sum (ib||cl) \hat{c}_a^\dagger \hat{c}_j^\dagger \hat{c}_d \hat{c}_k \\
&+ \sum (aj||kl) \hat{c}_a^\dagger \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k - \sum (aj||cd) \hat{c}_a^\dagger \hat{c}_c^\dagger \hat{c}_j^\dagger \hat{c}_d \\
&+ \sum (ab||kd) \hat{c}_a^\dagger \hat{c}_d \hat{c}_b \hat{c}_k - \sum (ij||kd) \hat{c}_j^\dagger \hat{c}_d \hat{c}_i \hat{c}_k \\
&+ \frac{1}{2} \sum (ib||kd) \hat{c}_d \hat{c}_b \hat{c}_i \hat{c}_k + \frac{1}{2} \sum (aj||cl) \hat{c}_a^\dagger \hat{c}_c^\dagger \hat{c}_i^\dagger \hat{c}_j^\dagger,
\end{aligned} \tag{3.52}$$

where

$$F_{r,s} = \langle r|\hat{h}|s \rangle + \sum (ii||rs) - \sum (ir||is) \tag{3.53}$$

is the matrix of the Fock operator.

**Proof** A lot of algebra. ♡

For us, the particle-hole representation is more a source of terminology than a practical aid for algebraic manipulations.

#### IV. Wick's Theorem (simplified version)

Wick's theorem refers to a previously determined determinant of Slater (the physical vacuum state),,

$$|\Phi\rangle = |123 \dots N\rangle. \tag{3.54}$$

We will also use the

**Index Convention**

$$\begin{array}{ccc}
\underbrace{abc \dots gh} & | & \underbrace{ijklmn} & | & \underbrace{opq \dots xyz} \\
\text{unoccupied orbitals} & & \text{occupied orbitals} & & \text{orbitales of unspecified type}
\end{array} \tag{3.55}$$

but not the particle-hole operators,  $\hat{c}_r$  and  $\hat{c}_s^\dagger$ , of the particle-hole representation.

**Definition** The *contraction* of two second-quantized operators (that is, of two creation and annihilation operators or of two creation operators or of two annihilation operators) are the numbers given by

$$\begin{aligned}
r^{(1)} s^{(1)} &= \langle \Phi|rs|\Phi\rangle = 0 \\
r^\dagger{}^{(1)} s^\dagger{}^{(1)} &= \langle \Phi|r^\dagger s^\dagger|\Phi\rangle = 0 \\
r^{(1)} s^\dagger{}^{(1)} &= \langle \Phi|rs^\dagger|\Phi\rangle = \delta_{r,s}(1 - n_s) \\
r^\dagger{}^{(1)} s^\dagger &= \langle \Phi|r^\dagger s|\Phi\rangle = \delta_{r,s} n_s.
\end{aligned} \tag{3.56}$$

To evaluate an expression like

$$\langle \Phi|b_1^{(1)} b_2^{(2)} b_3^{(1)} b_4^{(2)} b_5^{(3)} b_6^{(3)}|\Phi\rangle \tag{3.57}$$

where the  $b_i$  are creation and annihilation operators, it suffices to apply the following rules:

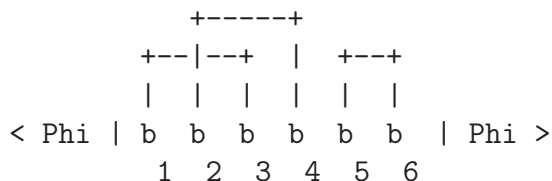
1. Anticommute the  $b_i$  without changing their order within each pair  $b_i^{(k)}b_j^{(k)}$ . In our example we get

$$-\langle \Phi | b_1^{(1)} b_3^{(1)} b_2^{(2)} b_4^{(2)} b_5^{(3)} b_6^{(3)} | \Phi \rangle. \tag{3.58}$$

*Handy Trick* : If we write

$$\langle \Phi | b_1^{(1)} b_2^{(2)} b_3^{(1)} b_4^{(2)} b_5^{(3)} b_6^{(3)} | \Phi \rangle \tag{3.59}$$

and connect each contracted pair with a line,



the sign after reordering is determined by whether the number of intersections of lines is odd or even.

2. Calculate the product

$$-b_1^{(1)} b_3^{(1)} b_2^{(2)} b_4^{(2)} b_5^{(3)} b_6^{(3)} \tag{3.60}$$

*Handy Trick*: There is no reason to carryout contractions that we know in advance will be zero. For example: all contractions between two creation operators  $r^\dagger s^\dagger$ , or two annihilation operators  $rs$ , any contraction between a pair  $ai^\dagger$  (instead of  $i^\dagger a$ ), and any contraction between a pair  $i^\dagger a$  (instead of  $ai^\dagger$ ).

Wick's Theorem

$$\langle \Phi | \hat{b}_1 \hat{b}_2 \dots \hat{b}_n | \Phi \rangle \tag{3.61}$$

is the suum of all nonzero contractions.

Examples.

- Evaluate  $\langle \Phi | \hat{v} | \Phi_i^a \rangle$ . Appendix ??.
- Evaluate  $\langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle$ . Appendix ??.

The number of nonzero contractions generated by Wick's theorem grows more rapidly with the degree of excitation of the determinants for 1-electron operators than for 2-electron operators:

Number of nonzero contractions generated by Wick's theorem for 1-electron integrals

	$\Phi$	S	D
$\Phi$	1	1	0
S	1	3	4
D	0	4	9

Number of nonzero contractions generated by Wick's theorem for 2-electron integrals

	$\Phi$	S	D
$\Phi$	2	4	4
S	4	14	32
D	4	32	114

Even if Wick's theorem saves us a lot of work, it is soon obvious in Appendix ?? that there is still a lot of work. It is tempting to think that the amount of work could be further reduced by using diagrammatic techniques. As diagrams were designed for perturbation theory, one nearly never sees them for the evaluation of CI matrix elements. On the other hand, after some thought, it does seem to be possible to write pseudo Goldstone diagrams for each term found using Wick's theorem. Diagrams of this type are shown in the appendix 4.3. To understand them, apply the usual rules for Goldstone diagrams. For example,

1. Each repulsion integrals is represented by dashed lines.
2. There is a prefactor of  $(-1)^{h+l}$  where  $h$  is the number of hole lines (downward lines) and  $l$  is the number of loops.
3. There is a prefactor of  $1/2$  for each vertical mirror plane.

On the other hand, in counter distinction with true Goldstone diagrams which have orbital energy difference denominators arising from perturbation theory, our pseudo Goldstone diagrams for CI matrix elements have no denominators. Initial excitations and final de-excitations have been represented by black boxes.

**Exercise:** Evaluate

- $\langle \Phi | \hat{h} | \Phi_i^a \rangle$ .
- $\langle \Phi_i^a | \hat{h} | \Phi_j^b \rangle$ .
- $\langle \Phi | \hat{h} | \Phi_{ij}^{ab} \rangle$ .
- $\langle \Phi_i^a | \hat{h} | \Phi_{jkl}^{abc} \rangle$ .
- $\langle \Phi_{ij}^{ab} | \hat{h} | \Phi_{kl}^{cd} \rangle$ .

### Recommended Reading

This section is partly based upon the contents of Ref. [14]. The Lazy Notation comes from the book [15]. The version of Wick's theorem given here is simplified. There are web pages oriented towards the coupled cluster method which discuss Wick's theorem in more detail and generality.

- Ref. [15]
- Ref. [14] pp. 89-97.

## 3.2 Hartree-Fock

Although the focus of this course is on excitations and excited states, we cannot avoid the ground state problem for two reasons. First of all, information about excited states is obtained in response theory by looking at the response of the ground state. Secondly, even if not using response theory to treat excited states, the nature of the excitation is always defined in relation to the ground state.

### I. Basic Equations

The Hartree-Fock (HF) method is the first approximation to the ground state of a closed (or half-closed) shell molecule. The idea of HF is to approximate the ground state by a single Slater determinant,

$$|\Phi\rangle = |1, 2, 3, \dots, N\rangle. \quad (3.62)$$

The orbitals are a solution of the orbital Schrödinger equation,

$$\hat{f}\psi_i = \epsilon_i\psi_i, \quad (3.63)$$

obtained by minimizing the energy,

$$E = \langle\Phi|\hat{H}|\Phi\rangle, \quad (3.64)$$

subject to the constraint that the orbitals are orthonormal,

$$\langle\psi_r|\psi_s\rangle = \langle r|s\rangle = \delta_{r,s}. \quad (3.65)$$

The energy expression is easy to obtain using Wick's theorem:

$$\begin{aligned} E &= \sum\langle p|\hat{h}|q\rangle\langle p^\dagger q\rangle + \frac{1}{2}\sum(pq||rs)\langle p^\dagger r^\dagger sq\rangle \\ &= \sum\langle p|\hat{h}|q\rangle\langle p^\dagger q\rangle + \frac{1}{2}\sum(pq||rs)\langle p^\dagger q\rangle\langle r^\dagger s\rangle - \frac{1}{2}\sum(pq||rs)\langle p^\dagger s\rangle\langle r^\dagger q\rangle \\ &= \sum\langle i|\hat{h}|i\rangle + \frac{1}{2}\sum(ii||jj) - \frac{1}{2}\sum(ij||ji), \end{aligned} \quad (3.66)$$

where the following index convention has been introduced:

$$\underbrace{abc\dots gh}_{\text{virtual orbitals}} \quad | \quad \underbrace{ijklmn}_{\text{occupied orbitals}} \quad | \quad \underbrace{opq\dots xyz}_{\text{orbitals with unspecified occupancy}} \quad (3.67)$$

The constrained minimization is carried out using the method of Lagrange multipliers. We minimize,

$$L = \sum\langle i|\hat{h}|i\rangle + \frac{1}{2}\sum(ii||jj) - \frac{1}{2}\sum(ij||ji) - \sum\epsilon_{i,j}(\langle i|j\rangle - \delta_{i,j}), \quad (3.68)$$

with the constraint (3.65). On minimizing,

$$\begin{aligned} 0 &= \frac{\delta L}{\delta\psi_i^*(\mathbf{x}_1)} \\ &= \hat{h}\psi_i(\mathbf{x}_1) + \sum_j n_j \int \frac{\psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2\psi_i(\mathbf{x}_1) \\ &\quad - \sum_j n_j\psi_j(\mathbf{x}_1) \int \frac{\psi_j^*(\mathbf{x}_2)\psi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 - \sum_j \epsilon_{i,j}\psi_j(\mathbf{x}_1), \end{aligned} \quad (3.69)$$

we obtain

$$\underbrace{(\hat{h} + \hat{J} - \hat{K})}_{\hat{f}}\psi_i = \sum_j \epsilon_{i,j}\psi_j. \quad (3.70)$$

the coulomb operator  $\hat{J}$  acts by,

$$\begin{aligned} \hat{J}\psi_i(\mathbf{x}_1) &= \sum_j \int \frac{\psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2\psi_i(\mathbf{x}_1) \\ &= \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\psi_i(\mathbf{x}_1), \end{aligned} \quad (3.71)$$

where

$$\rho(\mathbf{r}) = \sum \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}) \quad (3.72)$$

is the charge density. The coulomb operator represents the electrostatic interactions between the orbital  $\psi_i$  and the total charge density. As written here, the coulomb operator includes an important self-interaction error (physically an electron should not interact with itself.) This error is removed by the exchange operator  $\hat{K}$  which acts as,

$$\begin{aligned} \hat{K}\psi_i(\mathbf{x}_1) &= \sum_j \psi_j(\mathbf{x}_1) \int \frac{\psi_j^*(\mathbf{x}_2)\psi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \\ &= \int \frac{\gamma(\mathbf{x}_1, \mathbf{x}_2)}{r_{12}} \psi_i(\mathbf{x}_2) d\mathbf{x}_2, \end{aligned} \quad (3.73)$$

where

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) = \sum \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2), \quad (3.74)$$

is the one-electron reduced density matrix (1-RDM.) The exchange operator also represents the ‘‘Pauli force’’ – that is, the physical effect that same spin electrons avoid each other in space, thus reducing their mutual repulsion energy.

An important observation is that the density and the density matrix are each individually invariant to a unitary transformation of the occupied orbitals. This allows us to diagonalize the Lagrange multiplier matrix without changing the Fock matrix. The result is the Schrödinger equation for HF canonical orbitals,

$$\hat{f}\psi_i = \epsilon_i\psi_i. \quad (3.75)$$

Another important observation is that the occupied orbitals interact with  $N - 1$  electrons, in agreement with the observation of Koopmans that the canonical orbitals describe ionization. On the other hand, the virtual orbitals interact with  $N$  electrons in agreement with the idea that the virtual canonical orbitals describe electron attachment. Thus neither the occupied nor the unoccupied orbitals are well suited to describe excitation phenomena.

In what follows, we will compare the HF equations with the Kohn-Sham equations from pure DFT.

HF:

$$\begin{aligned} E_{HF} &= \sum \langle i | \hat{h} | i \rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 - \frac{1}{2} \int \int \frac{|\gamma(\mathbf{x}_1, \mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\ (\hat{h} + \hat{J} - \hat{K}) \psi_i &= \epsilon_i \psi_i \\ E_{HF} &= \sum_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 + \frac{1}{2} \int \int \frac{|\gamma(\mathbf{x}_1, \mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (3.76)$$

DFT:

$$\begin{aligned} E_{DFT} &= \sum \langle i | \hat{h} | i \rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 + \int \epsilon_{xc}[\rho](\mathbf{x})\rho(\mathbf{x}) d\mathbf{x} \\ (\hat{h} + \hat{J} + v_{xc}[\rho]) \psi_i &= \epsilon_i \psi_i \\ E_{DFT} &= \sum_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\ &+ \int (\epsilon_{xc}[\rho](\mathbf{x}) - v_{xc}[\rho](\mathbf{x})) \rho(\mathbf{x}) d\mathbf{x} \end{aligned} \quad (3.77)$$

In the case where we neglect correlation, we may hope that,

$$E_{DFT} \approx E_{HF}$$

$$-\frac{1}{2} \int \int \frac{|\gamma(\mathbf{x}_1, \mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \approx \int \epsilon_x[\rho](\mathbf{x}) \rho(\mathbf{x}) d\mathbf{x} \quad (3.78)$$

## II. Analytic Derivatives

An important aspect of ground state calculations is the ability to take analytic derivatives with respect to a parameter which we shall call  $\eta$ . The most important example of  $\eta$  is a geometric parameter. In that case, the analytic derivative is a force and, as such, is fundamental for automatic optimizations of molecular geometries and for *ab initio* molecular dynamics.

In quantum chemistry calculations, the molecular orbitals (MOs),  $\psi_s$ , are expanded in a basis of atomic orbitals (OAs),  $\chi_\mu$ ,

$$\psi_s(\mathbf{r}) = \sum \chi_\mu(\mathbf{r}) c_{\mu,s}. \quad (3.79)$$

When the parameter  $\eta$  varies, the AOs and the MO coefficients  $c_{\mu,s}$  in the AO basis will vary. We would like to separate these two types of  $\eta$ -dependent variations and, if possible, eliminate any derivatives with respect to the  $c_{\mu,s}$  since this costly to calculate. To carry out our program,

$$\begin{aligned} \frac{\partial \psi_s}{\partial \eta} &= \sum \frac{\partial \chi_\nu}{\partial \nu} c_{\mu,s} + \sum \chi_\mu \frac{\partial c_{\mu,s}}{\partial \eta} \\ &= \psi_s^\eta + \sum \psi_r U_{rs}^\eta. \end{aligned} \quad (3.80)$$

In general, the superscript  $\eta$  is reserved for a derivative at constant  $c_{\mu,s}$ . The only exception to this rule is the matrix  $U^\eta$ . In fact,

$$\begin{aligned} U_{rs}^\eta &= \sum_\mu \langle \psi_r | \chi_\mu \rangle \frac{\partial c_{\mu,s}}{\partial \eta} \\ &= \sum c_{\nu,r}^* S_{\nu,\mu} \frac{\partial c_{\mu,s}}{\partial \eta}, \end{aligned} \quad (3.81)$$

where,

$$S_{\nu,\mu} = \langle \chi_\nu | \chi_\mu \rangle, \quad (3.82)$$

is the AO overlap matrix.

We begin with a useful theorem.

**Theorem.** Suppose that  $\mathcal{O}$  is a functional of the MOs. Then

$$\frac{\partial \mathcal{O}}{\partial \eta} = \mathcal{O}^\eta + \sum U_{rs}^\eta \int \frac{\delta \mathcal{O}}{\delta \psi_s(1)} \psi_r(1) d1 + \sum U_{rs}^{\eta*} \int \frac{\delta \mathcal{O}}{\delta \psi_s^*(1)} \psi_r^*(1) d1. \quad (3.83)$$

**Proof.**

$$\begin{aligned} \frac{\partial \mathcal{O}}{\partial \eta} &= \mathcal{O}^\eta + \sum \frac{\partial \mathcal{O}}{\partial c_{\mu,s}} \frac{\partial c_{\mu,s}}{\partial \nu} + \sum \frac{\partial \mathcal{O}}{\partial c_{\mu,s}^*} \frac{\partial c_{\mu,s}^*}{\partial \nu} \\ &= \mathcal{O}^\eta + \sum \frac{\delta \mathcal{O}}{\delta \psi_s(1)} \frac{\partial \psi_s(1)}{\partial c_{\mu,s}} d1 \frac{\partial c_{\mu,s}}{\partial \nu} + \sum \int \frac{\delta \mathcal{O}}{\delta \psi_s^*(1)} \frac{\partial \psi_s^*(1)}{\partial c_{\mu,s}^*} d1 \frac{\partial c_{\mu,s}^*}{\partial \nu} \\ &= \mathcal{O}^\eta + \sum \frac{\delta \mathcal{O}}{\delta \psi_s(1)} \chi_\mu(1) d1 \frac{\partial c_{\mu,s}}{\partial \nu} + \sum \int \frac{\delta \mathcal{O}}{\delta \psi_s^*(1)} \chi_\mu^*(1) d1 \frac{\partial c_{\mu,s}^*}{\partial \nu} \\ &= \mathcal{O}^\eta + \sum \frac{\delta \mathcal{O}}{\delta \psi_s(1)} \psi_r(1) d1 U_{rs}^\eta + \sum \int \frac{\delta \mathcal{O}}{\delta \psi_s^*(1)} \psi_r^*(1) d1 U_{rs}^{\eta*} \end{aligned} \quad (3.84)$$



Applying the theorem to the energy gives,

$$\begin{aligned}
\frac{\partial E}{\partial \eta} &= E^\eta + \sum U_{rs}^\eta \int \frac{\delta E}{\delta \psi_s(1)} \psi_r(1) d1 + \sum U_{rs}^{\eta*} \int \frac{\delta E}{\delta \psi_s^*(1)} \psi_r^*(1) \\
&= E^\eta + \sum U_{rs}^\eta \int n_s(\hat{f}\psi_s(1))^* \psi_r(1) d1 + \sum U_{rs}^{\eta*} \int n_s(\hat{f}\psi_s(1)) \psi_r^*(1) d1 \\
&= E^\eta + \sum U_{rs}^\eta n_s f_{s,r} + \sum U_{rs}^{\eta*} n_s f_{r,s} \\
&= E^\eta + \sum U_{i,i}^\eta \epsilon_i + \sum U_{i,i}^{\eta*} \epsilon_i.
\end{aligned} \tag{3.85}$$

As,

$$S_{p,q} = \delta_{p,q}, \tag{3.86}$$

its application to the overlap matrix gives,

$$\begin{aligned}
0 &= \frac{\partial S_{p,q}}{\partial \eta} \\
&= S_{p,q}^\eta + \sum U_{r,s}^\eta \int \frac{\delta S_{p,q}}{\delta \psi_s(1)} \psi_r(1) d1 + \sum U_{r,s}^{\eta*} \int \frac{\delta S_{p,q}}{\delta \psi_s^*(1)} \psi_r^*(1) d1 \\
&= S_{p,q}^\eta + U_{p,q}^\eta + U_{q,p}^{\eta*}.
\end{aligned} \tag{3.87}$$

Thus we have the turnover rule,

$$U_{q,p}^{\eta*} = -U_{p,q}^\eta - S_{p,q}^\eta. \tag{3.88}$$

In the case that  $q = p$ , we have that

$$\Re U_{p,p}^\eta = -\frac{1}{2} S_{p,q}^\eta. \tag{3.89}$$

We can immediately apply this rule to the derivative of the energy to obtain,

$$\frac{\partial E}{\partial \eta} = E^\eta - \sum_i S_{i,i}^\eta \epsilon_i. \tag{3.90}$$

The first term is the Hellmann-Feynman force,

$$\begin{aligned}
\frac{\partial E}{\partial \eta} &= \left\langle \frac{\partial \Psi}{\partial \eta} | \hat{H} | \Psi \right\rangle + \langle \Psi | \frac{\partial \hat{H}}{\partial \eta} | \Psi \rangle + \left\langle \Psi | \hat{H} | \frac{\partial \Psi}{\partial \eta} \right\rangle \\
&= \left\langle \Psi | \frac{\partial \hat{H}}{\partial \eta} | \Psi \right\rangle + E \frac{\partial \langle \Psi | \Psi \rangle}{\partial \eta} \\
&= \left\langle \Psi | \frac{\partial \hat{H}}{\partial \eta} | \Psi \right\rangle \\
&= E^\eta.
\end{aligned} \tag{3.91}$$

The second term is the Pulay force. It is there because the AOs move with the nuclei and it is necessary to insure that the calculated forces are zero when the calculated energy is a minimum.

Sometimes we need to solve for  $U^\eta$ . To do this, begin with the relation,

$$f_{p,q} = \epsilon_p \delta_{p,q}. \tag{3.92}$$



For  $p \neq q$ ,

$$\begin{aligned} 0 &= \frac{\partial f_{p,q}}{\partial \eta} \\ &= f_{p,q}^\eta + \sum U_{rs}^\eta \int \frac{\delta f_{p,q}}{\delta \psi_s(1)} \psi_r(1) d1 + \sum U_{rs}^{\eta*} \int \frac{\delta f_{p,q}}{\delta \psi_s^*(1)} \psi_r^*(1). \end{aligned} \quad (3.93)$$

Now, by writing,

$$f_{p,q} = h_{p,q} + v_{p,q}^{SCF} \quad (3.94)$$

we can treat the HF and DFT cases simultaneously. We find after a bit of algebra that,

$$\begin{aligned} 0 &= \frac{\partial f_{p,q}}{\partial \eta} \\ &= f_{p,q}^\eta + U_{p,q}^\eta \epsilon_p + U_{q,p}^{\eta*} \epsilon_q + \sum U_{r,s}^\eta K_{pq,rs} + \sum U_{r,s}^{\eta*} K_{pq,rs}, \end{aligned} \quad (3.95)$$

where the coupling matrix is defined as,

$$\begin{aligned} v_{p,q}^{SCF} &= v_{p,q}^{SCF}[\gamma] \\ \gamma(1, 2) &= \sum \psi_r(1) P_{r,s} \psi_s^*(2) \\ K_{pq,rs} &= \frac{\partial v_{p,q}^{SCF}}{\partial P_{r,s}}. \end{aligned} \quad (3.96)$$

In the HF case,

$$K_{pq,rs} = (qp|f_H|sr) - (pr|f_H|sq). \quad (3.97)$$

In the DFT case,

$$K_{pq,rs} = (qp|f_H|sr) - (qp|f_{xc}|sr). \quad (3.98)$$

By applying the turnover rule, we find our first example of a coupled equation,

$$\sum [\delta_{p,s} \delta_{r,q} (\epsilon_p - \epsilon_q) + K_{pq,rs} + K_{pq,rs}] U_{r,s}^\eta = -f_{p,q}^\eta + S_{p,q}^\eta \epsilon_q + \sum K_{pq,rs} S_{s,r}^\eta. \quad (3.99)$$

### III. Ionization and Attachment Energies

We have already mentioned that occupied orbitals see  $N - 1$  electrons and virtual orbitals see  $N$  electrons in the HF model. These orbitals are preprepared to describe ionization. In the absence of relaxation, the ionization energy of the orbital  $\psi_i$  is given in HF by Koopmans' theorem,

$$\begin{aligned} -IP_i &= E(N) - E(N - 1) \\ &= \epsilon_i \\ &= \langle i|\hat{h}|i\rangle + \sum_j (ii||jj) - \sum_j (ij||ji). \end{aligned} \quad (3.100)$$

Similarly the electron attachment energy of the orbital  $\psi_a$  is given in HF by,

$$\begin{aligned} -EA_a &= E(N + 1) - E(N) \\ &= \epsilon_a \\ &= \langle a|\hat{h}|a\rangle + \sum_j (aa||jj) - \sum_j (aj||ja). \end{aligned} \quad (3.101)$$

It is interesting to compare these expressions with the corresponding DFT expressions. In DFT the occupied and virtual orbitals see the same potential, hence the same number of electrons. In this case, it is absolutely essential to take relaxation into account. One way to do this is with the  $\Delta$ SCF method. To calculate an ionization energy with the  $\Delta$ SCF method, one does an SCF calculation to obtain the ground state energy of the  $N$  electron system. Then one redoes the calculation with an electron removed from orbital  $\psi_i$  to obtain the energy of the system with  $N - 1$  electrons, and takes the difference of the two energies. In the case of the first ionization energy (the HOMO ionization energy), one is taking the difference of two ground state energies (for the  $N$ - and  $N - 1$ -electron systems respectively). The method is thus rigorous. This same energy also corresponds to exciting an electron to the continuum. In the case of other ionization energies, the  $\Delta$ SCF method has no rigorous basis, but is still found to be useful. One way to estimate  $\Delta$ SCF energies is by Slater's transition state method,

$$\begin{aligned}
 -IP_i &= E(N) - E(N - 1) \\
 &= \int_0^1 \frac{dE(N - 1 + \lambda)}{d\lambda} d\lambda \\
 &= \int_0^1 \epsilon_i(n_i = \lambda) d\lambda \\
 &\approx \epsilon_i(n_i = \frac{1}{2}),
 \end{aligned} \tag{3.102}$$

where we have used Janak's theorem,

$$\frac{\partial E}{\partial n_i} = \epsilon_i. \tag{3.103}$$

The conclusion is that minus the ionization potential is the orbital energy on condition that the orbital is only half full,

$$\begin{aligned}
 -IP_i &= \epsilon_i - \frac{1}{2} (ii|f_H|ii) + \langle i|v_{xc}^\uparrow[\rho_\uparrow - \frac{1}{2}\rho_i, \rho_\downarrow], \rho_\downarrow|i\rangle \\
 &\approx \epsilon_i - \frac{1}{2} (ii|f_H + f_{xc}^{\uparrow,\uparrow}|ii).
 \end{aligned} \tag{3.104}$$

The second term on the right is the relaxation energy of the  $N$ -electron system. Here,

$$\begin{aligned}
 f_H(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{r_{12}} \\
 f^{\sigma,\tau}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\delta^2 E_{xc}[\rho_\uparrow, \rho_\downarrow]}{\delta\rho_\sigma(\mathbf{r}_1)\delta\rho_\tau(\mathbf{r}_2)} \\
 E_{xc}[\rho + \delta\rho] &= E_{xc}[\rho] + \int \frac{\delta E_{xc}[\rho]}{\delta\rho(1)} \delta\rho(1) d1 + \frac{1}{2} \int \int \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(1)\delta\rho(2)} \delta\rho(1)\delta\rho(2) d1d2 \\
 &+ \frac{1}{6} \int \int \int \frac{\delta^3 E_{xc}[\rho]}{\delta\rho(1)\delta\rho(2)\delta\rho(3)} \delta\rho(1)\delta\rho(2)\delta\rho(3) d1d2d3 + \dots \\
 &= E_{xc}[\rho] + \int v_{xc}(1)\delta\rho(1) d1 + \frac{1}{2} \int \int f_{xc}(1, 2)\delta\rho(1)\delta\rho(2) d1d2 \\
 &+ \frac{1}{6} \int \int \int g_{xc}(1, 2, 3)\delta\rho(1)\delta\rho(2)\delta\rho(3) d1d2d3 + \dots.
 \end{aligned} \tag{3.105}$$

Similarly the electron attachment energy for the orbital  $\psi_a$  is,

$$\begin{aligned}
 -EA_a &= \epsilon_a + \frac{1}{2} (ii|f_H|ii) + \langle a|v_{xc}^\uparrow[\rho_\uparrow + \frac{1}{2}\rho_a, \rho_\downarrow], \rho_\downarrow|a\rangle \\
 &\approx \epsilon_a + \frac{1}{2} (aa|f_H + f_{xc}^{\uparrow,\uparrow}|aa).
 \end{aligned} \tag{3.106}$$

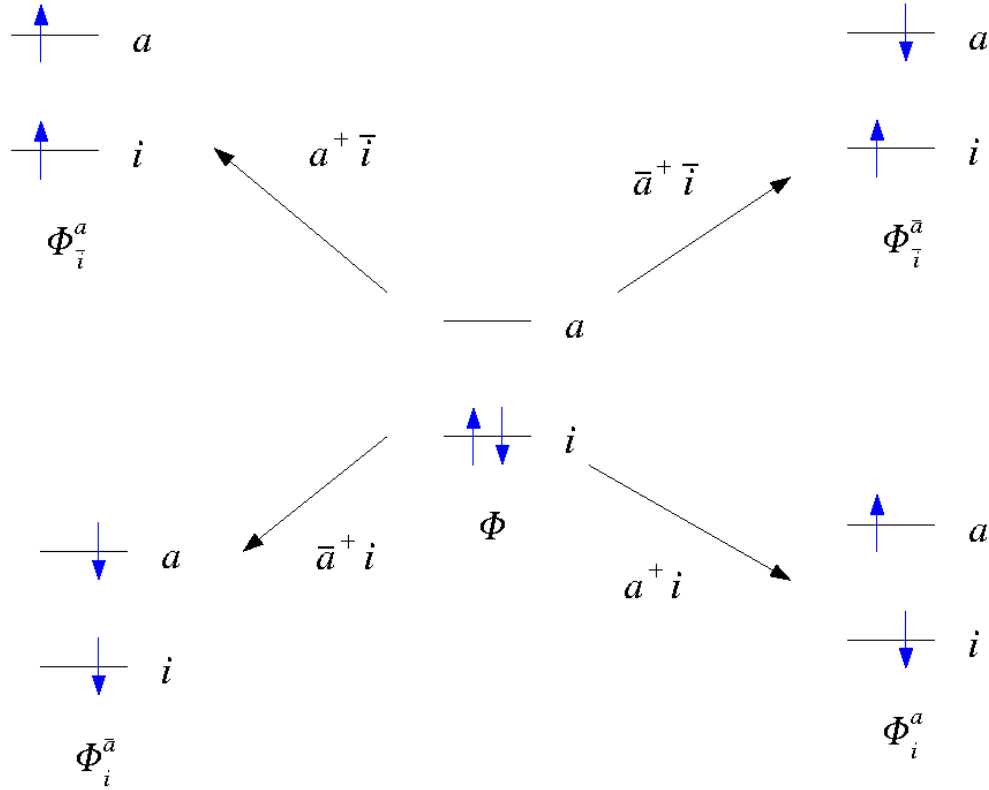


Figure 3.1: Single excitations with spin flip (left) and without spin flip (right).

#### IV. Excitation Energies

Consider the excitations shown in Fig. 3.1. Not all are eigenfunctions of  $\hat{S}^2$ . They must be recoupled to obtain,

$$\begin{aligned}
 \Psi_{S,M_S} &= \\
 \Psi_{0,0} &= \frac{1}{\sqrt{2}} (\Phi_i^a + \Phi_i^{\bar{a}}) \text{ Singlet} \\
 \Psi_{1,+1} &= \Phi_i^a \text{ Triplet} \\
 \Psi_{1,0} &= \frac{1}{\sqrt{2}} (\Phi_i^a - \Phi_i^{\bar{a}}) \text{ Triplet} \\
 \Psi_{1,-1} &= \Phi_i^{\bar{a}} \text{ Triplet} .
 \end{aligned} \tag{3.107}$$

In the absence of spin-orbit coupling, the three triplet states have the same energy. Thus, supposing that DFT is valid for the lowest state of each symmetry, we can obtain the energy of the first triplet by the  $\Delta$ SCF method.

In HF, that gives

$$\omega_T = \epsilon_a - \epsilon_i - (aa|f_H|ii) . \tag{3.108}$$

The energy of the singlet is more difficult because it does not correspond to a single-determinantal wave function. Nevertheless we can apply the multiplet sum method (MSM). In the present case, it

is particularly easy. The two states have the energies,

$$\begin{aligned} E_S &= \langle \Psi_{0,0} | \hat{H} | \Psi_{0,0} \rangle = \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle + \langle \Phi_i^a | \hat{H} \text{vert} \Phi_i^{\bar{a}} \rangle \\ E_T &= \langle \Psi_{1,0} | \hat{H} | \Psi_{1,0} \rangle = \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle - \langle \Phi_i^a | \hat{H} \text{vert} \Phi_i^{\bar{a}} \rangle. \end{aligned} \quad (3.109)$$

Thus,

$$E_S + E_T = 2 \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle. \quad (3.110)$$

Now,

$$E_T = \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle. \quad (3.111)$$

So

$$E_S = 2 \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle - \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle. \quad (3.112)$$

Finally applying this equation in HF, we get,

$$\omega_S = \epsilon_a - \epsilon_i + 2(ai|f_H|ia) - (aa|f_H|ii). \quad (3.113)$$

To obtain DFT excitation energies, we can once more use Slater's transition state method. To calculate the excitation energy for promoting an electron from orbital  $\psi_i$  to orbital  $\psi_a$ , we must excite half an electron and then take the orbital energy difference,

$$\begin{aligned} \omega_T &= \epsilon_a(n_a = n_{\bar{i}} = \frac{1}{2}) - \epsilon_i(n_a = n_{\bar{i}} = \frac{1}{2}) \\ &= \epsilon_a - \epsilon_i + \frac{1}{2} (aa - ii|f_H + f_{xc}^{\uparrow,\uparrow}|aa - ii) + (aa|f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}|ii) \\ &= -(EA_a - IP_i) - (aa|f_{xc}^{\uparrow,\downarrow}|ii) - (aa|f_H|ii). \end{aligned} \quad (3.114)$$

By using the MSM, we obtain

$$\omega_S = -(EA_a - IP_i) - (aa|2f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}|ii) - (aa|f_H|ii) \quad (3.115)$$

At least in some cases ( $H_2$  with a minimal basis set) these formulae give results in reasonable agreement with the results of  $\Delta$ SCF calculations (Fig. 3.2)

DFT/HF comparison:

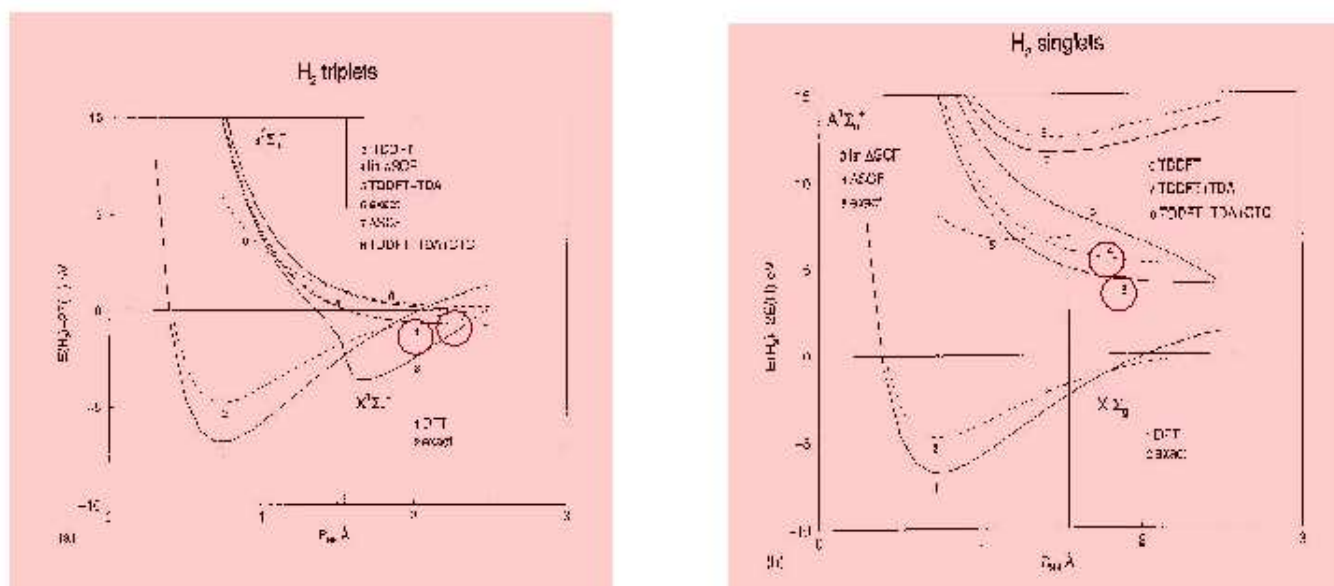
$$\begin{array}{l} \text{HF} \\ \omega_T = \epsilon_a - \epsilon_i - (aa|f_H|ii) \\ \omega_S = \epsilon_a - \epsilon_i + 2(ai|f_H|ia) - (aa|f_H|ii) \\ \text{DFT} \\ \omega_T = -(EA_a - IP_i) - (aa|f_{xc}^{\uparrow,\downarrow}|ii) - (aa|f_H|ii) \\ \omega_S = -(EA_a - IP_i) - (aa|2f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}|ii) - (aa|f_H|ii) \end{array} \quad (3.116)$$

To go from the DFT formulae to the HF formulae, it suffices to

- replace  $EA_a$  with  $-\epsilon_a$  and  $IP_i$  with  $-\epsilon_i$ .
- remove the  $f^{\uparrow,\downarrow}$  terms since these are the result of electron correlation
- replace  $(aa|f_{xc}^{\uparrow,\uparrow}|ii)$  with the negative of the exchange integral  $(ai|f_H|ia)$ .

Overall the procedure is quite logical.

## THE LINEARIZED THEORY IS NOT TOO BAD FOR $H_2$



M.E. Casida, F. Gutierrez, J. Guan, F.-X. Gadea, D.R. Salahub and J.-P. Daudey, *J. Chem. Phys.* **113**, 7062 (2000). “Charge-transfer correction for improved time-dependent local density approximation excited-state energy curves: Analysis within the two-level model with application to  $H_2$  and LiH”

Figure 3.2: Comparison of  $\Delta$ SCF MSM results with those obtained from the linearized formulae presented here.

### 3.3 CIS

The minimal method for treating excited states is the configuration interaction singles (CIS) method. We will find very similar formulae to those of CIS when we do LR-TDDFT with the Tamm-Dancoff approximation.

#### I. Basic Equations

The variational principle is applied to a trial function of the form

$$\Psi_I = \Phi C_0 + \sum_{i,a} a^\dagger_i \Phi C_i^a. \quad (3.117)$$

Minimizing

$$E = \frac{\langle \Psi_I | \hat{H} | \Psi_I \rangle}{\langle \Psi_I | \Psi_I \rangle} \quad (3.118)$$

gives (a bit symbolically),

$$\begin{bmatrix} \langle \Phi | \hat{H} | \Phi \rangle & \langle \Phi | \hat{H} | \Phi_j^b \rangle \\ \langle \Phi_i^a | \hat{H} | \Phi \rangle & \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle \end{bmatrix} \begin{pmatrix} C_0 \\ C_j^b \end{pmatrix} = E_I \begin{pmatrix} C_0 \\ C_i^a \end{pmatrix}. \quad (3.119)$$

Thanks to Wick's theorem, we can calculate the terms to find,

$$\begin{bmatrix} E_{HF} & f_{j,b} \\ f_{a,i} & A_{ia,jb} - \delta_{i,j} \delta_{ab} E_{HF} \end{bmatrix} \begin{pmatrix} C_0 \\ C_j^b \end{pmatrix} = E_I \begin{pmatrix} C_0 \\ C_i^a \end{pmatrix}. \quad (3.120)$$

The elements  $f_{a,i} = f_{j,b} = 0$  if we work with canonical HF orbitals (Brillouin's theorem). Thus the excitation problem is completely decoupled from the ground state and we can write,

$$\mathbf{A} \vec{C}_I = \omega_I \vec{C}_I, \quad (3.121)$$

where

$$\omega_I = E_I - E_{HF}. \quad (3.122)$$

The  $\mathbf{A}$  matrix can be directly determined using Wick's rules, but it is also interesting to determine it using the relation,

$$\begin{aligned} A_{ia,jb} &= \langle \Phi_i^a | \hat{H} - E_{HF} | \Phi_j^b \rangle \\ &= \langle \Phi | i^\dagger a [\hat{H}, b^\dagger j] | \Phi \rangle. \end{aligned} \quad (3.123)$$

Notice the presence of a commutator with  $\hat{H}$ , reminiscent of an equation of motion. There is thus the possibility of making a link with time-dependent theory ...

The commutator also has the very interesting property that it reduces the number of creation and annihilation operators by two. Thus,

$$\begin{aligned} [\hat{h}, b^\dagger j] &= \sum h_{p,q} [p^\dagger q, b^\dagger j] \\ &= \sum h_{p,q} (p^\dagger q b^\dagger j - b^\dagger j p^\dagger q) \\ &= \sum h_{p,q} (\delta_{q,b} p^\dagger j - p^\dagger b^\dagger q j - \delta_{j,p} b^\dagger q + b^\dagger p^\dagger j q) \\ &= \sum h_{p,q} (\delta_{q,b} p^\dagger j - \delta_{j,p} b^\dagger q) \\ &= \sum h_{p,b} p^\dagger j - \sum h_{j,p} b^\dagger q, \end{aligned} \quad (3.124)$$

and

$$\langle \Phi_i^a | \hat{h} | \Phi_j^b \rangle = \delta_{i,j} h_{a,b} - \delta_{a,b} h_{j,i}. \quad (3.125)$$

In a similar manner, one finds,

$$A_{ia,jb} = \delta_{i,j} \delta_{a,b} (\epsilon_a - \epsilon_i) + (ia|f_H|bj) - (ij|f_H|ba). \quad (3.126)$$

## II. Two-Orbital Model

In a two-orbital model, we only consider transitions from orbital  $i$  to orbital  $a$ , that is  $i \rightarrow a$  ( $i \uparrow \rightarrow a \uparrow$ ) and  $\bar{i} \rightarrow \bar{a}$  ( $i \downarrow \rightarrow a \downarrow$ ). The CIS matrix is then  $2 \times 2$ ,

$$\begin{bmatrix} \epsilon_a - \epsilon_i + (ia|f_H|ai) - (ii|f_H|aa) & (ia|f_H|ai) \\ (ia|f_H|ia) & \epsilon_a - \epsilon_i + (ia|f_H|ai) - (ii|f_H|aa) \end{bmatrix} \begin{pmatrix} C_i^a \\ C_{\bar{i}}^{\bar{a}} \end{pmatrix} = \omega \begin{pmatrix} C_i^a \\ C_{\bar{i}}^{\bar{a}} \end{pmatrix}. \quad (3.127)$$

There are two solutions. The triplet solution is,

$$\begin{aligned} \omega_T &= \epsilon_a - \epsilon_i - (ii|f_H|aa) \\ C_{\bar{i}}^{\bar{a}} &= -C_i^a = \frac{1}{\sqrt{2}}. \end{aligned} \quad (3.128)$$

The singlet solution is,

$$\begin{aligned} \omega_S &= \epsilon_a - \epsilon_i + 2(ia|f_H|ai) - (ii|f_H|aa) \\ C_{\bar{i}}^{\bar{a}} &= +C_i^a = \frac{1}{\sqrt{2}}. \end{aligned} \quad (3.129)$$

These are, in fact, the same solutions that we already found by the  $\Delta$ SCF multiplet sum method.

If we want to find the same results in DFT as already found with the  $\Delta$ SCF multiplet sum method, our  $\mathbf{A}$  must take the form,

$$\mathbf{A} = \begin{bmatrix} -(EA_a - IP_i) - (ii|f_H + f_{xc}^{\uparrow,\uparrow}|aa) & (ii|f_{xc}^{\uparrow,\downarrow} - f_{xc}^{\uparrow,\uparrow}|aa) \\ (ii|f_{xc}^{\uparrow,\downarrow} - f_{xc}^{\uparrow,\uparrow}|aa) & -(EA_a - IP_i) - (ii|f_H + f_{xc}^{\uparrow,\uparrow}|aa) \end{bmatrix}. \quad (3.130)$$

Its diagonalization gives the triplet solution,

$$\begin{aligned} \omega_T &= -(EA_a - IP_i) - (ii|f_H|aa) - (ii|f_{xc}^{\uparrow,\downarrow}|aa) \\ C_{\bar{i}}^{\bar{a}} &= -C_i^a = \frac{1}{\sqrt{2}}, \end{aligned} \quad (3.131)$$

and the singlet solution is,

$$\begin{aligned} \omega_S &= \epsilon_a - \epsilon_i - 2(ii|f_{xc}^{\uparrow,\uparrow}|aa) - (ii|f_H|aa) + (ii|f_{xc}^{\uparrow,\downarrow}|aa) \\ C_{\bar{i}}^{\bar{a}} &= +C_i^a = \frac{1}{\sqrt{2}}. \end{aligned} \quad (3.132)$$

The generalization to more than two orbitals is not obvious. One idea is perhaps,

$$A_{ia\sigma,jb\tau} = -\delta_{i,j} \delta_{a,b} \delta_{\sigma,\tau} (EA_a - IP_i) - \delta_{\sigma,\tau} (ij|f_H + f_{xc}^{\sigma,\sigma}|ab) + (ij|f_{xc}^{\sigma,\tau}|ab) - \frac{1}{2} [(ij|f_{xc}^{\sigma,\sigma}|ab) + (ij|f_{xc}^{\tau,\tau}|ab)], \quad (3.133)$$

but the way spin is treated is then not very natural.

### III. Davidson Diagonalization

The goal of the CIS method is to calculate excitation energies for large molecules, but the  $\mathbf{A}$  matrix can become very large. Fortunately it is possible to only determine the lowest eigenvalues and their associated eigenvectors using special iterative Krylov space methods. The matrix  $\mathbf{A}$  is never constructed but we need to know how to calculate the vector  $\mathbf{A}\mathbf{x}$  from the vector  $\mathbf{x}$  without ever constructing  $\mathbf{A}$ .

The most popular Krylov space method for CIS (and also for TDDFT) is the Davidson method. Suppose that we are interested in the lowest energy solution of

$$\mathbf{A}\mathbf{x} = a\mathbf{x}. \quad (3.134)$$

We will expand  $\mathbf{x}$  in a finite basis set,  $(\mathbf{x}_0, \mathbf{x}_1, \mathbf{x}_2, \dots)$ , which will be progressively expanded using perturbation theory. Here  $\mathbf{x}_0$  is a first estimation of  $\mathbf{x}$ , needed to begin the iterations. We write,

$$\mathbf{x} = \mathbf{x}_0 + \delta\mathbf{x}. \quad (3.135)$$

It is easy to deduce that

$$(\mathbf{A} - a)\delta\mathbf{x} = (a - \mathbf{A})\mathbf{x}_0. \quad (3.136)$$

We cannot simply invert  $(\mathbf{A} - a)$  to find  $\delta\mathbf{x}$ , except if we insert a projector,

$$\mathbf{Q} = \mathbf{1} - \mathbf{x}_0\mathbf{x}_0^\dagger. \quad (3.137)$$

Then

$$\delta\mathbf{x} = [\mathbf{Q}(a - \mathbf{A})\mathbf{Q}]^{-1} (\mathbf{A} - a)\mathbf{x}_0. \quad (3.138)$$

After normalization,  $\delta\mathbf{x}$  is our next vector  $\mathbf{x}_1$  that we will add to our finite basis set in order to improve our calculation. But the calculation of  $\delta\mathbf{x}$  is still too difficult unless we make further approximations. Fortunately  $\delta\mathbf{x}$  does not have to be very exact because we are just using it to generate a basis function. We can typically get away with the diagonal part,  $\mathbf{D}$ , of  $\mathbf{A}$  and we will use,

$$\delta\mathbf{x} = (a - \mathbf{D})^{-1}(a - \mathbf{A})\mathbf{x}_0 \quad (3.139)$$

as correction.

The full algorithm is,

1. find a first estimation of  $\mathbf{x}_0$
2. calculate the correction  $\delta\mathbf{x} = (a - \mathbf{D})^{-1}(a - \mathbf{A})\mathbf{x}_0$
3. if  $|\delta\mathbf{x}| < \epsilon$ , then the calculation is converged
4. otherwise, orthonormalize  $\delta\mathbf{x}$  with respect to  $\mathbf{x}_0$  to obtain  $\mathbf{x}_1$
5. make the matrix  $2 \times 2$  in the Krylov space,

$$\tilde{\mathbf{A}} = \begin{bmatrix} \mathbf{x}_0^\dagger \mathbf{A} \mathbf{x}_0 & \mathbf{x}_0^\dagger \mathbf{A} \mathbf{x}_1 \\ \mathbf{x}_1^\dagger \mathbf{A} \mathbf{x}_0 & \mathbf{x}_1^\dagger \mathbf{A} \mathbf{x}_1 \end{bmatrix} \quad (3.140)$$

6. solve  $\tilde{\mathbf{A}}\mathbf{c} = \tilde{a}\mathbf{c}$

7. update:  $\mathbf{x}_0 \leftarrow c_0\mathbf{x}_0 + c_1\mathbf{x}_1$



8. repeat until converged

To find the first several eigenvalues and eigenvectors, there is a block version of the Davidson algorithm.

You will almost always see Davidson iterations in your CIS, TDHF, and TDDFT calculations. As shown in Fig. 3.3, the results are essentially exact.

#### IV. Analytic Derivatives

travail en cours

#### IV. Static Exchange

One of the problems with CIS is that it is based upon HF orbitals which are predisposed to describe ionization and electron attachment, rather than excitation, phenomena. One way to correct this problem is called “static exchange” where the virtual orbitals are the empty orbitals taken from a calculation on the ionized molecule with an electron removed from the orbital  $\psi_i$ . Before the removal of this electron, the orbital  $\psi_i$  sees  $N - 1$  electrons and has the energy  $\epsilon_i$ . After removal of the electron from  $\psi_i$ , the virtual orbitals  $\psi_a$  see  $N - 1$  electrons and have the energies  $\epsilon_a(i^{-1})$ . The excited-state wave function is,

$$\Psi_I = \sum a^\dagger i \Phi C_{i,a}, \quad (3.141)$$

and the excitation energy is

$$\omega_I = \langle \Psi_I | \hat{H} | \Psi_I \rangle - \langle \Phi | \hat{H} | \Phi \rangle. \quad (3.142)$$

If we suppose that the orbitals  $\psi_a$  and  $\psi_i$  are orthogonal (which is not rigorously the case), then we can write that

$$A_{i a, j b} = \delta_{i, j} \delta_{a, b} (\epsilon_a(i^{-1}) - \epsilon_i) + (i a | f_H | b j). \quad (3.143)$$

In the two-orbital model, we remove the repulsion and exchange with the orbital  $\psi_i$  to obtain,

$$\epsilon_a(i^{-1}) = \epsilon_a - (i i | f_H | a a) + (i a | f_H | a i). \quad (3.144)$$

Thus,

$$\begin{aligned} \omega_T &= \epsilon_a(i^{-1}) - \epsilon_i - (i a | f_H | a i) \\ \omega_S &= \epsilon_a(i^{-1}) - \epsilon_i + (i a | f_H | a i). \end{aligned} \quad (3.145)$$

For a review of the static exchange method, see Ref. [16].

In DFT, as the occupied and virtual orbitals both see the same potential, we do not need to remove the repulsion with orbital  $\psi_i$ . The HF exchange must also be cancelled out but with a DFT exchange integral,

$$\epsilon_a(i^{-1}) \rightarrow \epsilon_a + (i a | f_x^{\uparrow, \uparrow} | a i) + (i a | f_H | a i). \quad (3.146)$$

The new excitation energies are

$$\begin{aligned} \omega_T &= \epsilon_a - \epsilon_i + (i a | f_x^{\uparrow, \uparrow} | a i) \\ \omega_S &= \epsilon_a - \epsilon_i + 2(i a | f_H | a i) + (i a | f_x^{\uparrow, \uparrow} | a i). \end{aligned} \quad (3.147)$$

This is exactly the (Tamm-Dancoff approximation) TDDFT result found in the absence of correlation.

Vertical Excitation Energies in eV (oscillator strength)

State	Full diagonalization <sup>a</sup>	Davidson (40 states) <sup>b</sup>	Davidson (30 states) <sup>b</sup>	Davidson (20 states) <sup>b,d</sup>	Davidson (10 states) <sup>b</sup>	Davidson (10 states) <sup>e</sup>
15	9.983579					
14	9.982837					
13	8.261105	8.261105	8.261103	8.261104		
12	8.237879	8.237889	8.237879	8.237880		
11	8.101488	8.101494	8.101489	8.101492		
10	7.514902	7.514902	7.514904	7.514908	7.514908	
9	7.336417 (0.300983)	7.336417 (0.300977)	7.336415 (0.300978)	7.336417 (0.300879)	7.336418 (0.300999)	
8	7.317097	7.317098	7.317097	7.317100	7.317099	
7	7.258573	7.258573	7.258573	7.258573	7.258575	
6	7.234619	7.234620	7.234621	7.234619	7.234623	
5	7.221868	7.221869	7.221870	7.221875	7.221871	7.221149
4	7.023707	7.023707	7.023707	7.023707	7.023709	7.044960
3	6.688117 (0.059847)	6.688117 (0.059828)	6.688117 (0.059847)	6.688121 (0.059683)	6.688117 (0.059882)	6.694128 (0.058550)
2	6.596621	6.596621	6.596621	6.596621	6.596626	6.606604
1	4.403895	4.403898	4.403895	4.403895	4.403898	4.574847
No. iterations		20	15	13	11	8
Memory	38MB	43MB	45MB	6MB	43MB	8MB
user time	38.24	14.52	14.49	13.01	7.77	8.15
system time	999.65	196.96	157.07	142.28	129.56	113.39

Figure 3.3: Example showing that the Davidson method gives the same answers as full diagonalization.

## 3.4 LR-TDHF

We have derived the CIS equations using the variational principle. It is also possible to find similar equations beginning with the dynamic response of the ground state. This may be a bit surprising. We begin with a single determinantal theory such as HF or Kohn-Sham DFT and what comes out are configuration interaction equations!

The equations for LR-TDHF and LR-TDDFT will be derived in this section. There are several ways to find the LR-TDHF equations (often called RPA equations in the Quantum Chemistry literature) and fewer ways to find the LR-TDDFT equations. We will follow here the treatment of Casida[1] which is based upon density matrices.

### I. Density Matrices

The one-electron reduced density matrix is

$$\gamma_{q,p} = \langle \Psi | p^\dagger q | \Psi \rangle. \quad (3.148)$$

The corresponding operator is

$$\hat{\gamma} = \sum |q\rangle \gamma_{q,p} \langle p|. \quad (3.149)$$

The kernel  $A(\mathbf{x}_1, \mathbf{x}_2)$  of an operator  $\hat{A}$  is defined as

$$(\hat{A}\psi)(\mathbf{x}_1) = \int A(\mathbf{x}_1, \mathbf{x}_2) \psi(\mathbf{x}_2) d\mathbf{x}_2, \quad (3.150)$$

where  $\psi$  is an arbitrary function. The kernel of the operator  $\hat{\gamma}$  is

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) = \sum \psi_q(\mathbf{x}_1) \gamma_{q,p} \psi_p^*(\mathbf{x}_2). \quad (3.151)$$

It can also be written as

$$\gamma(1, 1') = N \int \int \cdots \int \Psi(1, 2, 3, \dots, N) \Psi^*(1', 2, 3, \dots, N) d2d3 \cdots dN. \quad (3.152)$$

By abuse of language, the matrix, the operator, and the kernel are all called the density matrix.

Equation (3.148) is written in an orthonormal basis such as the set of molecular orbitals. In the atomic orbital basis set, we traditionally use a different notation, de notation,

$$\hat{\gamma} = \sum |\chi_\mu\rangle P_{\mu,\nu} \langle \chi_\nu|. \quad (3.153)$$

Here  $P$  is a capital  $\rho$ . The matrix elements of  $\hat{\gamma}$  in the same basis set are given by

$$\begin{aligned} \gamma_{\mu',\nu'} &= \sum \langle \chi_{\mu'} | \chi_\mu \rangle P_{\mu,\nu} \langle \chi_\nu | \chi_{\nu'} \rangle \\ \gamma &= \mathbf{SPS} \\ \mathbf{P} &= \mathbf{S}^{-1} \gamma \mathbf{S}^{-1}. \end{aligned} \quad (3.154)$$

The matrix  $\mathbf{P}$  is also called the density matrix.

The kernel of the HF exchange operator is easily expressed in terms of the density matrix,

$$K(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\delta_{\sigma,\sigma'} \frac{\gamma(\mathbf{r}\sigma, \mathbf{r}'\sigma')}{r_{12}}. \quad (3.155)$$

As the density is the diagonal element of the density matrix,

$$\rho_\sigma(\mathbf{r}) = \gamma(\mathbf{r}\sigma, \mathbf{r}\sigma), \quad (3.156)$$

the coulomb repulsion operator and the DFT exchange-correlation potential are also easily expressed in terms of the density matrix.

## II. Linear Response Equation

In HF and in DFT the density matrix of the unperturbed system is,

$$\begin{aligned}\gamma_\sigma(\mathbf{r}, \mathbf{r}') &= \sum \psi_{p\sigma}(\mathbf{r}) P_{pq\sigma} \psi_{p\sigma}(\mathbf{r}') \\ P_{pq\sigma} &= n_{p\sigma} \delta_{p,q}.\end{aligned}\quad (3.157)$$

Its response to a time-dependent electric field is,

$$\delta\gamma_\sigma(\mathbf{r}, \mathbf{r}') = \sum \psi_{p\sigma}(\mathbf{r}) \delta P_{pq\sigma}(\omega) \psi_{q\sigma}^*(\mathbf{r}'). \quad (3.158)$$

As

$$\psi_{i\sigma}(\mathbf{r}\omega) = \sum \psi_{p\sigma}(\mathbf{r}) \frac{\langle \psi_{p\sigma} | \hat{b}(\omega) | \psi_{i\sigma} \rangle}{\omega - (\epsilon_{p\sigma} - \epsilon_{i\sigma})}, \quad (3.159)$$

and as,

$$\delta\gamma_\sigma(\mathbf{r}, \mathbf{r}') = \sum \delta\psi_{i\sigma}(\mathbf{r}) n_i \psi_{i\sigma}^*(\mathbf{r}') + \sum \psi_{i\sigma}(\mathbf{r}) n_i \delta\psi_{i\sigma}^*(\mathbf{r}'), \quad (3.160)$$

then,

$$\delta P_{pq\sigma}(\omega) = \frac{n_{q\sigma} - n_{p\sigma}}{\omega - (\epsilon_{p\sigma} - \epsilon_{q\sigma})} \langle \psi_{p\sigma} | \hat{b}_{eff}(\omega) | \psi_{q\sigma} \rangle, \quad (3.161)$$

for

$$\hat{b}(t) = \hat{b} \cos(\omega t). \quad (3.162)$$

The reason for writing  $\hat{b}_{eff}(\omega)$  and not just  $\hat{b}(\omega)$  is that  $\hat{b}_{eff}(\omega)$  is the perturbation felt by the HF or DFT orbitals and not the applied field. The difference between these two perturbations is the response of the self-consistent field,

$$\hat{b}_{eff}(\omega) = \hat{b}(\omega) + \delta\hat{v}_{SCF}(\omega). \quad (3.163)$$

In terms of matrices,

$$b_{pq\sigma}^{eff}(\omega) = b_{pq\sigma}(\omega) + \sum K_{pq\sigma,rs\tau} \delta P_{rs\tau}(\omega), \quad (3.164)$$

where the coupling matrix is,

$$K_{pq\sigma,rs\tau} = \frac{\partial v_{pq\sigma}^{SCF}}{\partial P_{rs\tau}}. \quad (3.165)$$

In HF,

$$K_{pq\sigma,rs\tau} = (pq|f_H|rs) - \delta_{\sigma,\tau} (pr|f_H|sq). \quad (3.166)$$

In DFT,

$$K_{pq\sigma,rs\tau} = (pq|f_H|rs) + (pq|f_{xc}^{\sigma,\tau}|rs). \quad (3.167)$$

Thus we have that

$$\delta P_{pq\sigma}(\omega) = \frac{n_{q\sigma} - n_{p\sigma}}{\omega - (\epsilon_{p\sigma} - \epsilon_{q\sigma})} \left[ b_{pq\sigma}(\omega) + \sum K_{pq\sigma,rs\tau} \delta P_{rs\tau}(\omega) \right], \quad (3.168)$$

or

$$\sum_{rs\tau}^{n_{p\sigma} \neq n_{q\sigma}} \left[ \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} \frac{\omega - (\epsilon_{p\sigma} - \epsilon_{q\sigma})}{n_{q\sigma} - n_{p\sigma}} - K_{pq\sigma,rs\tau} \right] \delta P_{rs\tau}(\omega) = b_{pq\sigma}(\omega). \quad (3.169)$$

We can solve this equation at each frequency  $\omega$  and so calculate the response of each property  $a$  at that frequency. But we would like to go further and have an SOS-type formula so that we can extract excitation energies and their associated oscillator strengths.

The first step is to separate the hole-particle (hp) and particle-hole (pq) components to obtain the two equations,

$$\begin{aligned}
& \sum_{rst}^{n_{p\sigma} > n_{q\sigma}} \left[ \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} \frac{\omega - (\epsilon_{p\sigma} - \epsilon_{q\sigma})}{n_{q\sigma} - n_{p\sigma}} - K_{pq\sigma,rs\tau} \right] \delta P_{rs\tau}(\omega) \\
& - \sum_{rst}^{n_{p\sigma} > n_{q\sigma}} K_{pq\sigma,rs\tau} \delta P_{sr\tau}(\omega) = b_{pq\sigma}(\omega) \\
& \sum_{rst}^{n_{p\sigma} > n_{q\sigma}} \left[ \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} \frac{\omega - (\epsilon_{q\sigma} - \epsilon_{p\sigma})}{n_{p\sigma} - n_{q\sigma}} - K_{qp\sigma,rs\tau} \right] \delta P_{sr\tau}(\omega) \\
& - \sum_{rst}^{n_{p\sigma} > n_{q\sigma}} K_{qp\sigma,rs\tau} \delta P_{rs\tau}(\omega) = b_{qp\sigma}(\omega). \tag{3.170}
\end{aligned}$$

For occupation numbers equal to 0 or 1, we have the matrix form,

$$\begin{aligned}
& \left\{ \omega \begin{bmatrix} -\delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} & 0 \\ 0 & +\delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} \end{bmatrix} - \begin{bmatrix} \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} (\epsilon_{q\sigma} - \epsilon_{p\sigma}) + K_{pq\sigma,rs\tau} & K_{pq\sigma,rs\tau} \\ K_{qp\sigma,rs\tau} & \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} (\epsilon_{q\sigma} - \epsilon_{p\sigma}) + K_{qp\sigma,rs\tau} \end{bmatrix} \right\} \\
& \times \begin{pmatrix} \delta P_{rs\tau}(\omega) \\ \delta P_{sr\tau}(\omega) \end{pmatrix} = \begin{pmatrix} \delta b_{pq\tau}(\omega) \\ \delta b_{qp\tau}(\omega) \end{pmatrix}. \tag{3.171}
\end{aligned}$$

As  $\delta P_{pq\sigma}(\omega) = \delta P_{qp\sigma}^*(\omega)$  and as, for real orbitals,  $K_{pq\sigma,rs\tau} = K_{qp\sigma,rs\tau}$ , we have,

$$\begin{aligned}
& \left\{ \omega \begin{bmatrix} -\delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} & 0 \\ 0 & +\delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} \end{bmatrix} - \begin{bmatrix} \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} (\epsilon_{q\sigma} - \epsilon_{p\sigma}) + K_{pq\sigma,rs\tau} & K_{pq\sigma,rs\tau} \\ K_{qp\sigma,rs\tau} & \delta_{\sigma,\tau} \delta_{p,r} \delta_{q,s} (\epsilon_{q\sigma} - \epsilon_{p\sigma}) + K_{qp\sigma,rs\tau} \end{bmatrix} \right\} \\
& \times \begin{pmatrix} \delta P_{rs\tau}(\omega) \\ \delta P_{sr\tau}^*(\omega) \end{pmatrix} = \begin{pmatrix} \delta b_{pq\tau}(\omega) \\ \delta b_{qp\tau}^*(\omega) \end{pmatrix}. \tag{3.172}
\end{aligned}$$

With the definitions,

$$\begin{aligned}
A_{ia\sigma,jb\tau} &= \delta_{\sigma,\tau} \delta_{i,j} \delta_{a,b} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + K_{ia\sigma,jb\tau} \\
B_{ia\sigma,jb\tau} &= K_{ia\sigma,bj\tau}, \tag{3.173}
\end{aligned}$$

we have

$$\left\{ \omega \begin{bmatrix} -1 & 0 \\ 0 & +1 \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \right\} \begin{pmatrix} \delta \mathbf{P}(\omega) \\ \delta \mathbf{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{b}(\omega) \\ \mathbf{b}^*(\omega) \end{pmatrix}. \tag{3.174}$$

At an excitation frequency, the response the density matrix is infinite even if the perturbation is finite. This means that the excitation frequency must satisfy,

$$\omega_I \begin{bmatrix} -1 & 0 \\ 0 & +1 \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} = 0. \tag{3.175}$$

Put another way, the excitation frequencies must satisfy the pseudo-eigenvalue problem,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} +1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}. \tag{3.176}$$

One way to do this is to rewrite the equation as

$$\Omega \mathbf{F}_I = \omega_I^2 \mathbf{F}_I, \quad (3.177)$$

with

$$\begin{aligned} \Omega &= (\mathbf{A} - \mathbf{B})^{1/2} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{1/2} \\ \mathbf{F}_I &= (\mathbf{A} - \mathbf{B})^{-1/2} (\mathbf{X}_I + \mathbf{Y}_I). \end{aligned} \quad (3.178)$$

So much for the excitation energies, but what about the oscillator strengths? Let us seek an SOS formula for the dynamic polarizability. After a unitary transformation,

$$\left\{ \omega \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - \begin{bmatrix} \mathbf{A} + \mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} - \mathbf{B} \end{bmatrix} \right\} \begin{pmatrix} \Re e \delta \mathbf{P}(\omega) \\ -i \Im m \delta \mathbf{P}(\omega) \end{pmatrix} = \begin{pmatrix} \Re e \mathbf{b}(\omega) \\ -i \Im \mathbf{b}(\omega) \end{pmatrix}. \quad (3.179)$$

We can solve this equation for a real perturbation to find,

$$(\Re e \delta \mathbf{P})(\omega) = (\mathbf{A} - \mathbf{B})^{1/2} (\omega_I^2 \mathbf{1} - \Omega)^{-1} (\mathbf{A} - \mathbf{B})^{1/2} \mathbf{b}(\omega). \quad (3.180)$$

For the dynamic polarizability,

$$\alpha_{x,z}(\omega) = -2 \mathbf{x}^\dagger (\mathbf{A} - \mathbf{B})^{1/2} (\omega_I^2 \mathbf{1} - \Omega)^{-1} (\mathbf{A} - \mathbf{B})^{1/2} \mathbf{z}. \quad (3.181)$$

We can then directly apply the SOS theorem to find that the oscillator strength is

$$\begin{aligned} f_I^x &= 2\omega_I |\langle \Psi_0 | \hat{x} | \Psi_I \rangle|^2 \\ &= 2 |\mathbf{x}^\dagger (\mathbf{A} - \mathbf{B})^{1/2} \mathbf{F}|^2 \\ f_I &= \frac{1}{3} (f_I^x + f_I^y + f_I^z). \end{aligned} \quad (3.182)$$

### III. Tamm-Dancoff Approximation

The Tamm-Dancoff approximation (TDA) is

$$\mathbf{A} \mathbf{X}_I = \omega_I \mathbf{X}_I. \quad (3.183)$$

The TDA often gives results which are a good approximation to full LR-TDHF results aroundd the equilibrium geometry of the molecule. Ditto for the TDA in LR-TDDFT.

In the case of LR-TDHF, the TDA result is CIS. In the case of LR-TDDFT we have something new. To understand this better, let us look at the two-orbital model. We have,

$$\begin{bmatrix} \epsilon_a - \epsilon_i + (ia|f_H|ai) + (ia|f_{xc}^{\uparrow,\uparrow}|ai) & (ia|f_H + f_{xc}^{\uparrow,\downarrow}|ai) \\ (ia|f_H + f_{xc}^{\uparrow,\downarrow}|ai) & \epsilon_a - \epsilon_i + (ia|f_H|ai) + (ia|f_{xc}^{\uparrow,\uparrow}|ai) \end{bmatrix} \begin{pmatrix} C_i^a \\ C_i^{\bar{a}} \end{pmatrix} = \omega \begin{pmatrix} C_i^a \\ C_i^{\bar{a}} \end{pmatrix}. \quad (3.184)$$

There are two solutions. The triplet solution is,

$$\begin{aligned} \omega_T &= \epsilon_a - \epsilon_i + (ia|f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}|ai) \\ C_i^{\bar{a}} &= -C_i^a = \frac{1}{\sqrt{2}}. \end{aligned} \quad (3.185)$$

The singlet solution is,

$$\begin{aligned}\omega_S &= \epsilon_a - \epsilon_i + 2(ia|f_H|ai) + (ia|f_{xc}^{\uparrow,\uparrow} + f_{xc}^{\uparrow,\downarrow}|ai) \\ C_i^{\bar{a}} &= +C_i^a = \frac{1}{\sqrt{2}}.\end{aligned}\tag{3.186}$$

We have already given a physical interpretation noting the analogy with static exchange.

#### IV. Analytic Derivatives

work in progress

#### V. Triplet Instabilities

work in progress





# Chapter 4

## Appendices

### 4.1 The Dirac $\delta$ Function

The Dirac  $\delta$  function is defined in terms of the integral of its product with an arbitrary function,  $f$ , as,

$$f(x_0) = \int_{-\infty}^{\infty} \delta(x - x_0) f(x) dx. \quad (4.1)$$

It follows that,

$$f(0) = \int_{-\infty}^{\infty} \delta(x) f(x) dx. \quad (4.2)$$

Doing this requires that,

$$\delta(x) = \begin{cases} 0 & ; x \neq 0 \\ +\infty & ; x = 0 \end{cases}, \quad (4.3)$$

and,

$$\int_{-\infty}^{\infty} \delta(x) dx = 1. \quad (4.4)$$

If we insist on a rigorous terminology,  $\delta(x)$  is a distribution rather than a function because of its divergence at  $x = 0$ .

The  $\delta$  function may be obtained as the limits of different functions when a small real positive number,  $\eta$ , goes to zero ( $\eta \rightarrow 0^+$ ). Particularly useful representations include: a Gaussian,

$$\delta(x) = \lim_{\eta \rightarrow 0^+} \frac{1}{\eta\sqrt{\pi}} e^{-x^2/\eta^2}; \quad (4.5)$$

a Lorentzian,

$$\delta(x) = \lim_{\eta \rightarrow 0^+} \frac{\eta}{\pi(x^2 + \eta^2)}; \quad (4.6)$$

and the oscillating function,

$$\delta(x) = \lim_{\eta \rightarrow 0^+} \frac{\sin(x/\eta)}{\pi x}. \quad (4.7)$$

The  $\delta$  function has several interesting properties (see for example Ref. [12] p. 57) that follow from its defining integral. For example, the  $\delta$  function is even,

$$f(0) = \int_{-\infty}^{+\infty} \delta(x) f(x) dx$$

$$\begin{aligned}
&= \int_{-\infty}^{+\infty} \delta(x) f(-x) dx \\
&= \int_{+\infty}^{-\infty} \delta(-x) f(x) (-dx) \\
&= \int_{-\infty}^{+\infty} \delta(-x) f(x) dx,
\end{aligned} \tag{4.8}$$

hence

$$\delta(-x) = \delta(x). \tag{4.9}$$

Other relations include,

$$\begin{aligned}
\delta'(x) &= -\delta'(x) \\
x\delta(x) &= 0 \\
x\delta'(x) &= -\delta(x) \\
\delta(ax) &= \frac{1}{a}\delta(x) \quad a > 0 \\
\delta(x^2 - a^2) &= \frac{1}{2a} [\delta(x - a) + \delta(x + a)] \quad a > 0 \\
\int_{-\infty}^{+\infty} \delta(a - x)\delta(x - b) dx &= \delta(a - b) \\
f(x)\delta(x - a) &= f(a)\delta(x - a).
\end{aligned} \tag{4.10}$$

## 4.2 Fourier Transforms

According to the Fourier transform theorem (for continuous Fourier transforms),

$$\begin{aligned}
\tilde{f}(\nu) &= \int_{-\infty}^{+\infty} e^{+2\pi i\nu t} f(t) dt \\
f(t) &= \int_{-\infty}^{+\infty} e^{-2\pi i\nu t} \tilde{f}(\nu) d\nu.
\end{aligned} \tag{4.11}$$

It follows that,

$$\begin{aligned}
f(t) &= \int_{-\infty}^{+\infty} e^{-2\pi i\nu t} \left( \int_{-\infty}^{+\infty} e^{+2\pi i\nu t'} f(t') dt' \right) d\nu \\
&= \int_{-\infty}^{+\infty} \left( \int_{-\infty}^{+\infty} e^{+2\pi i\nu(t'-t)} d\nu \right) f(t') dt',
\end{aligned} \tag{4.12}$$

and thus that,

$$\int_{-\infty}^{+\infty} e^{+2\pi i\nu(t-t_0)} d\nu = \delta(t - t_0). \tag{4.13}$$

In particular,

$$\int_{-\infty}^{+\infty} e^{+2\pi i\nu t} d\nu = \delta(t). \tag{4.14}$$

This last relation is a powerful mnemonic for the Fourier transform theorem, but cannot be considered as rigorous because of the problems associated with integrating unity from minus infinity to plus infinity when  $t = 0$  and of integrating an oscillating function over the same range when  $t \neq 0$ .

On the other hand, we can make the same relation rigorous by introducing convergence parameters and taking the limit that the parameters become infinitely small,

$$\begin{aligned}
\int_{-\infty}^{+\infty} e^{+2\pi i \nu t} d\nu &= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^0 e^{+2\pi i \nu(t-i\eta)} d\nu + \lim_{\eta \rightarrow 0^+} \int_0^{+\infty} e^{+2\pi i \nu(t+i\eta)} d\nu \\
&= \lim_{\eta \rightarrow 0^+} \left[ \frac{e^{+2\pi i \nu(t-i\eta)}}{2\pi i(t-i\eta)} \right]_{-\infty}^0 + \lim_{\eta \rightarrow 0^+} \left[ \frac{e^{+2\pi i \nu(t+i\eta)}}{2\pi i(t+i\eta)} \right]_0^{+\infty} \\
&= \lim_{\eta \rightarrow 0^+} \left( -\frac{i}{2\pi} \right) \left[ \frac{1}{t-i\eta} - \frac{1}{t+i\eta} \right] \\
&= \lim_{\eta \rightarrow 0^+} \left( -\frac{i}{2\pi} \right) \frac{(t+i\eta) - (t-i\eta)}{t^2 + \eta^2} \\
&= \lim_{\eta \rightarrow 0^+} \left( -\frac{i}{2\pi} \right) \frac{+2i\eta}{t^2 + \eta^2} \\
&= \lim_{\eta \rightarrow 0^+} \frac{\eta}{\pi(t^2 + \eta^2)} \\
&= \delta(t),
\end{aligned} \tag{4.15}$$

where we have used that fact that the  $\delta$  function can be obtained as the limit of a an infinitely narrow Lorentzian line shape (Sec. 4.1). While the convergence parameter trick may shock a mathematician, it is very useful in physics. We will often use it in response theory to eliminate transient response in favor of adiabatic response.

A second theorem concerns the convolution of two functions,

$$(f \circ g)(t) = \int_{-\infty}^{+\infty} f(t-t')g(t') dt'. \tag{4.16}$$

Its Fourier transform is,

$$\begin{aligned}
(\widetilde{f \circ g})(\nu) &= \int_{-\infty}^{+\infty} e^{+2\pi i \nu t} \left[ \left( \int_{-\infty}^{+\infty} e^{-2\pi i \nu'(t-t')} \tilde{f}(\nu') d\nu' \right) \left( \int_{-\infty}^{+\infty} e^{-2\pi i \nu'' t'} \tilde{g}(\nu'') d\nu'' \right) dt \right] dt \\
&= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[ \int_{-\infty}^{+\infty} e^{+2\pi i(\nu-\nu')t} dt \right] \left[ \int_{-\infty}^{+\infty} e^{+2\pi i(\nu'-\nu'')t'} dt' \right] \tilde{f}(\nu') \tilde{g}(\nu'') d\nu' d\nu'' \\
&= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta(\nu-\nu') \delta(\nu'-\nu'') \tilde{f}(\nu') \tilde{g}(\nu'') d\nu' d\nu'' \\
&= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta(\nu-\nu') \delta(\nu-\nu'') \tilde{f}(\nu') \tilde{g}(\nu'') d\nu' d\nu'' \\
&= \tilde{f}(\nu) \tilde{g}(\nu).
\end{aligned} \tag{4.17}$$

In physics, we are often sloppy and simply drop the tilda ( $\sim$ ). The Fourier transform is then understood through the variable of the function,

$$\begin{aligned}
f(\nu) &= \int_{-\infty}^{+\infty} e^{+2\pi i \nu t} f(t) dt \\
f(t) &= \int_{-\infty}^{+\infty} e^{-2\pi i \nu t} f(\nu) d\nu.
\end{aligned} \tag{4.18}$$

Also in physics, the Fourier transforms are not always formulated in a symmetric manner. Thus instead of using the  $t \leftrightarrow \nu$  transform, we can rewrite the same theorems with the  $t \leftrightarrow \omega$  transform,

$$f(\omega) = \int_{-\infty}^{+\infty} e^{+i\omega t} f(t) dt$$

$$\begin{aligned}
f(t) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} f(\omega) d\omega \\
\delta(t-t') &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{+i\omega(t-t')} d\omega \\
(f \circ g)(t) &= \int_{-\infty}^{+\infty} f(t-t')g(t') dt' \\
(f \circ g)(\omega) &= f(\omega)g(\omega),
\end{aligned} \tag{4.19}$$

or with the  $t \leftrightarrow E$  transform,

$$\begin{aligned}
f(E) &= \int_{-\infty}^{+\infty} e^{+iEt/\hbar} f(t) dt \\
f(t) &= \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{-iEt/\hbar} f(E) dE \\
\delta(t-t') &= \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{+iE(t-t')/\hbar} dE \\
(f \circ g)(t) &= \int_{-\infty}^{+\infty} f(t-t')g(t') dt' \\
(f \circ g)(E) &= f(E)g(E),
\end{aligned} \tag{4.20}$$

We will most often use the  $t \leftrightarrow \omega$  transform.

### 4.3 Repulsion Integrals Evaluated Using Wick's Theorem

#### 4.3.1 Appendix: Evaluation of $\langle \Phi | \hat{v} | \Phi_i^a \rangle$ Using Wick's Theorem

Evaluate  $\langle \Phi | \hat{v} | \Phi_i^a \rangle$  where

$$\Phi_i^a = a^\dagger i \Phi \tag{4.21}$$

is a single excitation. (This integral is basic to Brillouin's theorem.) As

$$\langle \Phi | \hat{v} | \Phi_i^a \rangle = \frac{1}{2} \sum (rs || tu) \langle \Phi | r^\dagger t^\dagger u s a^\dagger i | \Phi \rangle, \tag{4.22}$$

we see that we must evaluate  $\langle \Phi | r^\dagger t^\dagger u s a^\dagger i | \Phi \rangle$ . By using the method of connecting lines we have the following nonzero contractions,

$$\begin{array}{l}
\begin{array}{cccccc}
+ & + & & + & & \\
< r & t & u & s & a & i >
\end{array} \\
\\
\begin{array}{l}
+-----+ +++ \\
| +--|-|-|---+ \quad 3 \text{ intersections } \Rightarrow \text{ minus} \\
|+ |+ | | |+ | \\
= < r & t & u & s & a & i > \quad (1)
\end{array} \\
\\
\begin{array}{l}
+----+ \\
+-----|-+ | \\
| +--|-|-|---+ \quad 4 \text{ intersections } \Rightarrow \text{ plus}
\end{array}
\end{array}$$

$$\begin{array}{c}
|+ | + | | | + | \\
+ < r t u s a i > \quad (2)
\end{array}$$

$$\begin{array}{c}
+---+ +--+ \\
+--|--| - | - | --- \quad 4 \text{ intersections } \Rightarrow \text{ plus} \\
|+ | + | | | + | \\
+ < r t u s a i > \quad (3)
\end{array}$$

$$\begin{array}{c}
+-----+ \\
| \quad + - | - + \\
+--|--| - | - | --- \quad 5 \text{ intersections } \Rightarrow \text{ minus} \\
|+ | + | | | + | \\
+ < r t u s a i > \quad (4)
\end{array}$$

Hence

$$\begin{array}{c}
+ \quad + \quad + \\
< r t u s a i >
\end{array}$$

$$\begin{array}{c}
+---+ +---+ +--+ \\
|+ | | + | | | + \\
= - r u t i s a \quad (1)
\end{array}$$

$$\begin{array}{c}
+---+ +---+ +--+ \\
|+ | | + | | | + \\
+ r s t i u a \quad (2)
\end{array}$$

$$\begin{array}{c}
+---+ +---+ +--+ \\
|+ | | + | | | + \\
+ r i t u s a \quad (3)
\end{array}$$

$$\begin{array}{c}
+---+ +---+ +--+ \\
|+ | | + | | | + \\
- r i t s u a \quad (4)
\end{array}$$

We have that,

$$\langle \Phi | r^\dagger t^\dagger u s a^\dagger i | \Phi \rangle = -\delta_{r,u} n_u \delta_{t,i} \delta_{s,a} + \delta_{r,s} n_s \delta_{t,i} \delta_{u,a} + \delta_{r,i} \delta_{t,u} n_u \delta_{s,a} - \delta_{r,i} \delta_{t,s} n_s \delta_{u,a}. \quad (4.23)$$

So

$$\begin{aligned}
\langle \Phi | \hat{v} | \Phi_i^a \rangle &= \frac{1}{2} \sum (rs || tu) [-\delta_{r,u} n_u \delta_{t,i} \delta_{s,a} + \delta_{r,s} n_s \delta_{t,i} \delta_{u,a} + \delta_{r,i} \delta_{t,u} n_u \delta_{s,a} - \delta_{r,i} \delta_{t,s} n_s \delta_{u,a}] \\
&= \frac{1}{2} [-\sum (ja || ij) + (jj || ia) + (ia || jj) - (ij || ja)] \\
&= \sum (ia || jj) - \sum (ij || ja) \\
&= J_{i,a} - K_{i,a}.
\end{aligned} \quad (4.24)$$

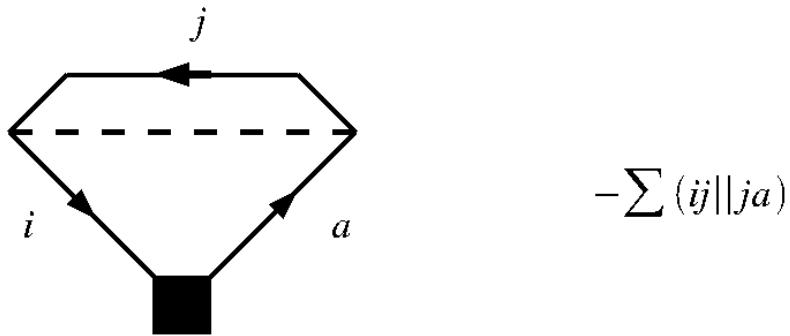
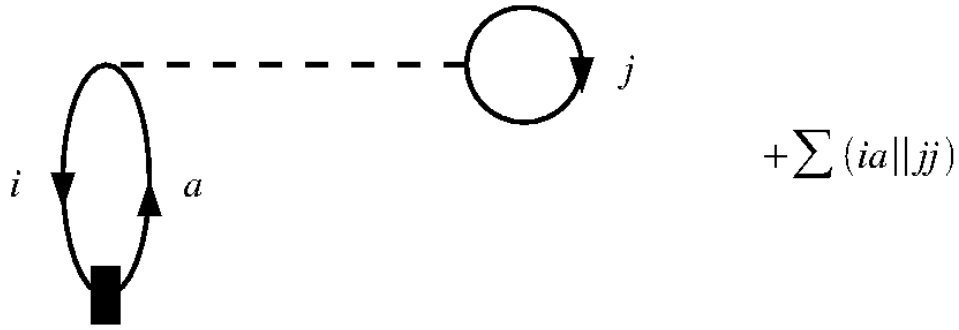


Figure 4.1: Pseudo Goldstone diagram development of the integral  $\langle \Phi | \hat{v} | \Phi_i^a \rangle$ .

The diagrammatic development is given in Fig. 4.1.

### 4.3.2 Appendix: Evaluation of $\langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle$ Using Wick's Theorem

Evaluation of  $\langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle$ .

$$\begin{array}{l}
 + \quad + \quad + \quad + \\
 \langle i \text{ a r t u s b j} \rangle \\
 \\
 +-----+ \\
 | +-----+ | \\
 | | +-----+ | | \\
 | | | +--+ | | | \\
 | + | | + | + | | | + | \\
 = \langle i \text{ a r t u s b j} \rangle \quad 0 \text{ intersections} \Rightarrow \text{plus} \quad (1)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | +-----+ | \\
 | | +-----+ | | \\
 | | +-|-+ | | | \\
 | + | | + | + | | | + | \\
 + \langle i \text{ a r t u s b j} \rangle \quad 1 \text{ intersections} \Rightarrow \text{minus} \quad (2)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | +-+ +-+ +-+ | \\
 | + | | + | + | | | + | \\
 + \langle i \text{ a r t u s b j} \rangle \quad 0 \text{ intersections} \Rightarrow \text{plus} \quad (3)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | +-----+ | \\
 | +-+ +-|-+ | | \\
 | + | | + | + | | | + | \\
 + \langle i \text{ a r t u s b j} \rangle \quad 1 \text{ intersections} \Rightarrow \text{minus} \quad (4)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | +-----+ | \\
 | +-|-+ +-|-+ | \\
 | + | | + | + | | | + | \\
 + \langle i \text{ a r t u s b j} \rangle \quad 2 \text{ intersections} \Rightarrow \text{plus} \quad (5)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | +-----+ | \\
 | +-|-+ | +-+ | \\
 | + | | + | + | | | + | \\
 + \langle i \text{ a r t u s b j} \rangle \quad 1 \text{ intersections} \Rightarrow \text{minus} \quad (6)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 +---|-----+ | \\
 | | +-----|-|-+
 \end{array}$$

$$\begin{array}{c}
 | \quad | \quad | \quad +-- \quad | \quad | \quad | \\
 |+ \quad | \quad |+\quad| \quad | \quad |+\quad| \\
 + \langle i \quad a \quad r \quad t \quad u \quad s \quad b \quad j \rangle
 \end{array}
 \quad 3 \text{ intersections } \Rightarrow \text{ minus}
 \quad (7)$$

$$\begin{array}{c}
 +-----+ \\
 +----|----+ \quad | \\
 | \quad +--|---|----+ \quad | \\
 | \quad | \quad | \quad +--|-- \quad | \quad | \\
 |+ \quad | \quad |+\quad| \quad | \quad |+\quad| \\
 + \langle i \quad a \quad r \quad t \quad u \quad s \quad b \quad j \rangle
 \end{array}
 \quad 4 \text{ intersections } \Rightarrow \text{ plus}
 \quad (8)$$

$$\begin{array}{c}
 +-----+ \\
 | \quad \quad \quad +--|-----+ \\
 | \quad +---|---|----+ \quad | \\
 | \quad | \quad +--|---|-- \quad | \quad | \\
 |+ \quad | \quad |+\quad| \quad | \quad |+\quad| \\
 + \langle i \quad a \quad r \quad t \quad u \quad s \quad b \quad j \rangle
 \end{array}
 \quad 5 \text{ intersections } \Rightarrow \text{ minus}
 \quad (9)$$



$$\begin{array}{l}
 +-----+ \\
 | \quad +---|----+ \\
 | \quad +---|---|--+ | \\
 | \quad | +-|--+ | | | \\
 |+ | |+|+| | |+| \\
 + \langle i \ a \ r \ t \ u \ s \ b \ j \rangle \quad 4 \text{ intersections } \Rightarrow \text{ plus} \quad (10)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 +-----|--+ \quad | \\
 | \quad +--+ | | +--+ | \\
 |+ | |+|+| | |+| \\
 + \langle i \ a \ r \ t \ u \ s \ b \ j \rangle \quad 1 \text{ intersections } \Rightarrow \text{ minus} \quad (11)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | \quad +---|-----+ \\
 | \quad +-|--+ | +--+ | \\
 |+ | |+|+| | |+| \\
 + \langle i \ a \ r \ t \ u \ s \ b \ j \rangle \quad 2 \text{ intersections } \Rightarrow \text{ plus} \quad (12)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | \quad +---|----+ \\
 | \quad +--+ | +-|--+ | \\
 |+ | |+|+| | |+| \\
 + \langle i \ a \ r \ t \ u \ s \ b \ j \rangle \quad 2 \text{ intersections } \Rightarrow \text{ plus} \quad (13)
 \end{array}$$

$$\begin{array}{l}
 +-----+ \\
 | \quad +-----|----+ \\
 | \quad +-|--+ +-|--+ | \\
 |+ | |+|+| | |+| \\
 + \langle i \ a \ r \ t \ u \ s \ b \ j \rangle \quad 3 \text{ intersections } \Rightarrow \text{ minus} \quad (14)
 \end{array}$$

Hence

$$\begin{array}{l}
 + \ + \ + \ + \\
 \langle i \ a \ r \ t \ u \ s \ b \ j \rangle
 \end{array}$$

$$\begin{array}{l}
 +--+ +--+ +--+ +--+ \\
 |+ | | |+ |+ | |+ | \\
 = \ i \ j \ a \ b \ r \ s \ t \ u \quad (1)
 \end{array}$$

$$\begin{array}{l}
 +--+ +--+ +--+ +--+ \\
 |+ | | |+ |+ | |+ | \\
 - \ i \ j \ a \ b \ r \ u \ t \ s \quad (2)
 \end{array}$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 + & i & j & a & r & t & u & s & b
 \end{array} \quad (3)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 - & i & j & a & r & t & s & u & b
 \end{array} \quad (4)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 + & i & j & a & t & r & s & u & b
 \end{array} \quad (5)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 - & i & j & a & t & r & u & s & b
 \end{array} \quad (6)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 - & i & s & a & b & r & j & t & u
 \end{array} \quad (7)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 + & i & u & a & b & r & j & t & s
 \end{array} \quad (8)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 - & i & u & a & b & r & s & t & j
 \end{array} \quad (9)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & |+| \\
 + & i & s & a & b & r & u & t & j
 \end{array} \quad (10)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 - & i & u & a & r & t & j & s & b
 \end{array} \quad (11)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 + & i & s & a & r & t & j & u & b
 \end{array} \quad (12)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 + & i & s & a & r & t & j & u & b
 \end{array} \quad (13)$$

$$\begin{array}{cccc}
 +---+ & +-+ & +---+ & +---+ \\
 |+| & | |+ & |+| & | |+ \\
 - & i & s & a & t & r & j & u & b
 \end{array} \quad (14)$$

So

$$\begin{aligned}
& \langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle \\
&= \frac{1}{2} \sum (rs || tu) \delta_{i,j} \delta_{a,b} \delta_{r,s} n_s \delta_{t,u} n_u \quad (1) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,j} \delta_{a,b} \delta_{r,u} n_u \delta_{t,s} n_s \quad (2) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{i,j} \delta_{a,r} \delta_{t,u} n_u \delta_{s,b} \quad (3) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,j} \delta_{a,t} \delta_{t,s} n_s \delta_{u,b} \quad (4) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{i,s} \delta_{a,t} \delta_{r,s} n_s \delta_{u,b} \quad (5) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,j} \delta_{a,t} \delta_{r,u} n_u \delta_{s,b} \quad (6) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,s} \delta_{a,b} \delta_{r,j} \delta_{t,u} n_u \quad (7) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{i,u} \delta_{a,b} \delta_{r,j} \delta_{t,s} n_s \quad (8) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,u} \delta_{a,b} \delta_{r,s} n_s \delta_{t,j} \quad (9) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{i,s} \delta_{a,b} \delta_{r,u} n_u \delta_{t,j} \quad (10) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,u} \delta_{a,r} \delta_{s,b} \delta_{t,j} \quad (11) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{a,t} \delta_{s,b} \delta_{r,j} \delta_{i,u} \quad (12) \\
&+ \frac{1}{2} \sum (rs || tu) \delta_{i,s} \delta_{a,r} \delta_{u,b} \delta_{t,j} \quad (13) \\
&- \frac{1}{2} \sum (rs || tu) \delta_{i,s} \delta_{a,t} \delta_{u,b} \delta_{r,j} \quad (14). \tag{4.25}
\end{aligned}$$

or

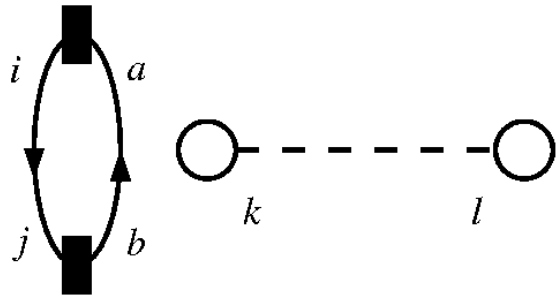
$$\begin{aligned}
& \langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle \\
&= \delta_{i,j} \delta_{a,b} \frac{1}{2} \sum (kk || ll) \quad (1) \\
&- \delta_{i,j} \delta_{a,b} \frac{1}{2} \sum (kl || lk) \quad (2) \\
&+ \delta_{i,j} \frac{1}{2} \sum (ab || kk) \quad (3) \\
&- \delta_{i,j} \frac{1}{2} \sum (ak || kb) \quad (4) \\
&+ \delta_{i,j} \frac{1}{2} \sum (kk || ab) \quad (5) \\
&- \delta_{i,j} \frac{1}{2} \sum (kb || ak) \quad (6) \\
&- \delta_{a,b} \frac{1}{2} \sum (ji || kk) \quad (7)
\end{aligned}$$

$$\begin{aligned}
& + \delta_{a,b} \frac{1}{2} \sum (jk||ki) \quad (8) \\
& - \delta_{a,b} \frac{1}{2} \sum (kk||ji) \quad (9) \\
& + \delta_{a,b} \frac{1}{2} \sum (ki||jk) \quad (10) \\
& - \frac{1}{2} (ab||ji) \quad (11) \\
& + \frac{1}{2} (jb||ai) \quad (12) \\
& + \frac{1}{2} (ia||jb) \quad (13) \\
& - \frac{1}{2} (ji||ab) \quad (14) .
\end{aligned} \tag{4.26}$$

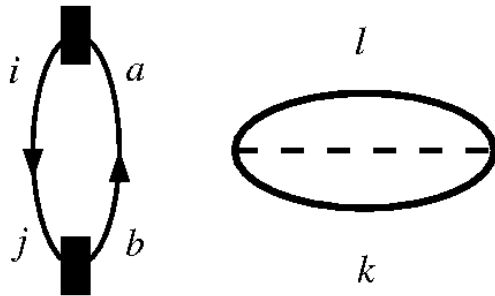
Donc

$$\begin{aligned}
\langle \Phi_i^a | \hat{v} | \Phi_j^b \rangle & = \\
& = \delta_{i,j} \delta_{a,b} \frac{1}{2} \left[ \sum (kk||ll) - \sum (kl||lk) \right] \\
& + \delta_{i,j} [J_{a,b} - K_{a,b}] \\
& - \delta_{a,b} (J_{j,i} - K_{j,i}) \\
& - (ab||ji) + (jb||ai) .
\end{aligned} \tag{4.27}$$

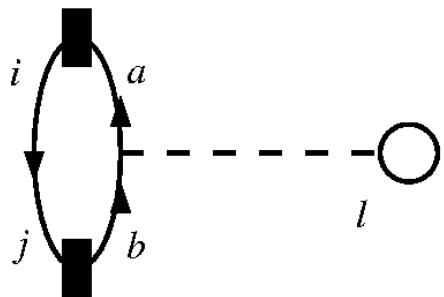
The diagrammatic development is shown in Fig. 4.2.



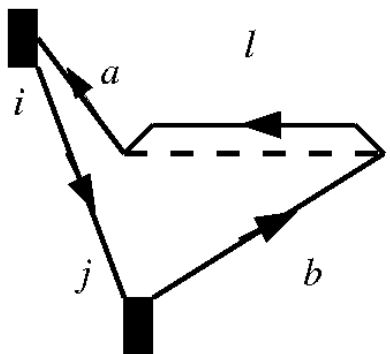
$$+\frac{1}{2}\delta_{i,j}\delta_{a,b}\sum(kk||ll)$$



$$-\frac{1}{2}\delta_{i,j}\delta_{a,b}\sum(kl||lk)$$



$$+\delta_{i,j}\sum(ab||ll)$$



$$-\delta_{i,j}\sum(al||bl)$$



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