

An overview of the RPA from the Quantum Chemistry perspective

Mark E. Casida^{1,*}

¹ *Laboratoire de Chimie Théorique (LCT), Département de Chimie Moléculaire (DCM, UMR CNRS/UJF 5250), Institut de Chimie Moléculaire de Grenoble (ICMG, FR-2607), Université Joseph Fourier (Grenoble I), 301 rue de la Chimie, BP 53, F-38041 Grenoble Cedex 9, FRANCE.*

* *corresponding author: mark.casida@ujf-grenoble.fr*

One way to understand the place of the RPA in Quantum Chemistry is to take a trip into the past. Physical chemists/chemical physicists (who I shall just call *chemists* for the purposes of this talk) have a lot in common with condensed matter physicists, atomic physicists, and (sometimes surprisingly) with nuclear physicists (I will just call these others collectively *physicists* in this talk.) Indeed the famous physical chemist, Robert Bunson (remember the Bunson burner?) once wrote that “*Ein Chemiker, der nicht gleichzeitig Physiker ist, ist gar nichts*” (“A chemist who is not at the same time a physicist is nothing at all.”) But chemists are generally, but not exclusively, concerned with moving nuclei and in particular making and breaking of chemical bonds, typically in finite systems (molecules.) Before the advent of computers sometime in the 1960s, some chemists thought being able to carry out Hartree-Fock molecular orbital calculations would solve most of the important chemical problems. But during the 1970s it became important to solve the correlation problem (i.e., to find the energy difference between the true solution to the electronic Schrödinger equation and the Hartree-Fock solution.) Some chemists began to try out many-body perturbation theory (MBPT) which had proven successful in physics and to adapt it to their needs. Exchange diagrams were rapidly added to the RPA to give RPAE or RPAX which finally became simply the RPA once again, but is different from that in, say, solid state physics because the chemists’ RPA includes exchange diagrams. Reasons for including exchange in Quantum Chemistry will be reviewed. MBPT going beyond the RPA was also developed into a fine art for the calculation of excitation spectra. Also connections were made between RPA solutions and stability criteria for Hartree-Fock solutions. For some purposes, chemists realized that the Tamm-Dancoff approximation (CIS for “configuration interaction singles”) is more accurate than the original RPA, something which still sometimes seems to shock our physicist breatheren. In the 1980s analytic gradients became important for automatic optimization of molecular geometries and it is not too surprising that such techniques were also developed for excited states. RPA analytic gradients also allowed a more correct calculation of certain excited-state properties such as dipole moments. However the use of the RPA to get ground state energies was largely, but not entirely, neglected. In the 1990s, chemists learned about time-dependent density-functional theory (TDDFT) and that it could be cast in the form of RPA equations (also different from the physicists’ RPA equations). Much of the pre-TDDFT RPA ideas could be carried over to TDDFT applications. However finding the optimal interface between density-functional ideas and MBPT is an active and very stimulating area of research, with seemingly many facets left to explore in years to come. One such area which will be touched upon is learning how to obtain improved correlation energies from TDDFT through the fluctuation-dissipation theorem. Another aspect (and one which perhaps can be addressed by this group) is the increasing need to harmonize chemical and physical approximations as we approach the same nano regime from two different directions (top-down and bottom-up.)