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REGULAR ARTICLE

Current functional theory for multi-electron configuration

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Abstract The density functional theory (DFT) formalism is reformulated into a framework of currents so as to give the energy a parameter dependent behaviour, e.g., time. This "current" method is aimed at describing the transition of electrons from one orbital to another and especially from the ground state to an excited state and extended to the relativistic region in order to include magnetic fields which is relevant especially for heavy metallic compounds. The formalism leads to a set of coupled first order partial differential equations to describe the time evolution of atoms and molecules. The application of the method to ZnO and H_2O to calculate the occupation probabilities of the orbitals lead to the results that compare favorably with those obtained from DFT. Furthermore, evolution equations for electrons in both atoms and molecules can be derived. Applications to specific examples of small molecules (being metallo-oxides and water) are mentioned at the end.

Keywords Density functional theory · Current DFT · Continuity equations

1 Introduction

Density functional theory (DFT) as formulated by Hohenberg and Kohn [1] and Sham [2], plays a prominent role of being the most used framework for performing quantum calculations of large molecular systems such as bio-molecules. However, electronic calculations of larger electron systems are difficult to carry out in a quantum mechanical setting with present days techniques [3–7]. They comprise for example the standard DFT computer programs, that have been very successful in dealing with smaller molecules. This is also due to the fact that the many-body Schrödinger equation is very complicated to solve since it involves many coupled partial differential equations of second order. We shall, instead, be using the equations for electronic currents and the corresponding continuity equations that, with the help of vector algebra, lead to a set of coupled first order partial deferential equations to describe the time evolution of multi-atomic molecules [8].

2 Formalism of multi-atomic molecular configurations

The following section presents an alternative to the standard DFT for the description of electron motions or states of molecules. DFT, developed particularly by Kohn and Hohenberg [1] and Sham [2] has proved efficient in many cases, and its use needs no further justification. Since then, many other comprehensive presentations and treatment have been given in the literature, e.g., Refs. [9, 10] in the large review [11]. In the following sections, the "current" formulation is introduced for electrons together with nuclei [12].

Dedicated to Professor Sandor Suhai on the occasion of his 65th birthday and published as part of the Suhai Festschrift Issue.

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2.1 Single electron description

The motion of the nuclei is mainly described by classical trajectories, whereas the density functionals are used to describe the electrons. We shall mostly use atomic units. The densities of electrons we shall, as usual, denote by n and the corresponding Schrödinger many-particle wave function by $\Psi(t)$. As in the standard literature about electronic calculations, we look at the $n(\mathbf{r},t)$ as evolving from an initial state

$$|\Psi_0\rangle = |\Psi(t_0)\rangle \tag{1}$$

determined by the Schrödinger equation

$$i\partial\Psi(t)/\partial t = \hat{H}(t)\Psi(t) \tag{2}$$

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{U} \tag{3}$$

$$\hat{V}(t) = \sum_{i=1}^{N} v(\mathbf{r}_i, t) \tag{4}$$

$$\hat{T} = \sum_{i=1}^{N} (-1/2)\nabla_i^2 \tag{5}$$

$$\hat{U} = 1/2 \sum_{i,j,i\neq j}^{N} 1/|\mathbf{r}_i - \mathbf{r}_j| \tag{6}$$

where V is an external potential (from nuclei) on electrons, U their mutual repulsion. The last term is by far the most difficult to handle. It is obviously not small compared to the other terms. The method suggested in [13], however, facilitates the treatment of just that term.

We shall assume that a local single particle potential, $v_s[n](\mathbf{r}, t)$ exists, which reproduces the time-dependent density

$$n(\mathbf{r}, t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r}, t)|^2 \tag{7}$$

with orbitals satisfying the Kohn–Sham (KS) or Schrödinger equation

$$\left(i\partial/\partial t + \nabla^2/2 - v_s[n](\mathbf{r}, t)\right)\phi_j(\mathbf{r}, t) = 0 \tag{8}$$

Generally

$$v_s[n](\mathbf{r}, t) = v(\mathbf{r}, t)) + \int \mathrm{d}^3r' n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'| + v_{xc}[n](\mathbf{r}, t) \tag{9}$$

where (9) *defines* the time-dependent xc-(exchange-correlation)-potential (see Appendix 1). A general matrix element of $v_s[n]$, corresponding to a transition from single particle state i to single particle state j

$$\langle\phi_j|v_s[n]|\phi_i\rangle \tag{10}$$

can be viewed as a sum over the single particle constituents (j') of n in the *second* term of (9)

$$v_s[n] = \int \mathrm{d}^3r' n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'| = \int \mathrm{d}^3r' \sum_{j'} |\phi_j'|^2|/|\mathbf{r} - \mathbf{r}'| \tag{11}$$

which can again be considered as the trace of the more general matrix

$$\mathrm{trace}[v_s[n]_{i',j'}] = \mathrm{trace} \int \mathrm{d}^3r' \phi_{i'}^* \phi_{j'}/|\mathbf{r} - \mathbf{r}'| \tag{12}$$

The idea is to use the Schrödinger equation, satisfied by all ϕ_m, and then derive from that the continuity equation for single particle electron densities

$$\partial n(\mathbf{r}, t)/\partial t = -\nabla\mathbf{j}(\mathbf{r}, t) \tag{13}$$

to introduce, instead of the electron transition densities, $n_{i,j}$, the corresponding *transition current densities*, see also [10, 11].

The main point is to use the time-dependent Schrödinger equation and, as the consequence of it, the continuity equation to eliminate the single particle densities in favour of similar *longitudinal* single particle currents

$$\frac{\partial\rho_{ki}}{\partial t} = i\frac{\mathrm{div}_r\mathbf{j}_{ki}}{E_k - E_i}\hbar \tag{14}$$

$n(r,t)$ and $j(r,t)$ are operators acting on state vectors i and j. Since our equation can be separated in a time-dependent and a space dependent partial differential equation, the densities can again be eliminated. The single particle energies E_i related to the state i, etc. are here replaced by the separation constants e_i, etc., and also the denominators $E_{ki}/\hbar^2$ should be replaced by $e_{ki} = e_k - e_i$. Remember $\mathbf{r}_- = |\mathbf{r} - \mathbf{r}'|$.

We may, as explained in Appendix 2, introduce the *longitudinal* currents

$$\mathbf{j}^L(\mathbf{r}) = -\nabla_r \int \mathrm{d}r'^3 \mathrm{div}_{r'}\mathbf{j}(\mathbf{r}')/|4\pi\mathbf{r}_-| \tag{15}$$

and by a partial integration we get the general Coulomb matrix element, connecting the transition densities $n_{ki}(\mathbf{r})$, $n_{jh}(\mathbf{r}')$:

$$I_{ki;jh} = \int \mathrm{d}^3r\left(\mathbf{j}_{ki}^L \cdot \mathbf{j}_{jh}^L\right)4\pi/e_{ki}e_{jh} \tag{16}$$

and the similar equation for the transverse component $\mathbf{j}_{ki}^T$. Here again the longitudinal and transverse currents in a spherical system take simple forms which can be expressed by means of vector spherical harmonics. A longitudinal field can be written:

$$\begin{aligned}\mathbf{L}_{J,M} = \nabla([\Phi^J]^{\mathrm{long}} Y_{J,M}) = -\sqrt{(J+1)/(2J+1)} \\ \times (\mathrm{d}/\mathrm{d}r - (J+0)/r)[\Phi^J]^{\mathrm{long}} Y_{J,J+1,M} \\ + \sqrt{(J+0)/(2J+1)}(\mathrm{d}/\mathrm{d}r + (J+1)/r) \\ \times [\Phi^J]^{\mathrm{long}} Y_{J,J-1,M}\end{aligned} \tag{17}$$

Analogously, a transverse field can be written

$$\begin{aligned}\mathbf{T}_{J,M} = \sqrt{(J+0)/(2J+1)} \\ \times (\mathrm{d}/\mathrm{d}r - (J+0)/r)\left[\Phi^J\right]^{\mathrm{tran}} Y_{J,J+1,M} \\ + \sqrt{(J+1)/(2J+1)} \\ \times (\mathrm{d}/\mathrm{d}r - (J+1)/r)\left[\Phi^J\right]^{\mathrm{tran}} Y_{J,J-1,M}\end{aligned} \tag{18}$$

This is not the only transverse field; any field where the vector spherical harmonics are of the type

$$Y_{J,J,M} \tag{19}$$

is also transverse. Already here the magnetic quantum numbers, M, are occurring together with the total spin, J. The total Fermion vector density with quantum numbers [J,l,M], where l is different from J, may be written as $\mathbf{A}_{J,l,M} = \mathbf{L}_{J,l,M} + \mathbf{T}_{J,l,M}$ The occurrence of e_{ki}, etc. in the denominators seems somewhat inconvenient since, whenever $e_k = e_i$, these denominators become zero. The corresponding numerators become also zero, however. The construction of a general transition current, containing both longitudinal and transverse components, from the single particle electron wave functions in spherical symmetric fields, is demonstrated in Appendix 2. The vector spherical harmonics, which are eigenfunctions of an angular momentum **J** with magnetic components **M**, given by addition of an orbital angular momentum **L** and a unit angular momentum **S**, eigenvectors **e**, are expressed as

$$\mathbf{Y}_{J,L,M} = \sum_{m,q} Y_{L,m}(\Omega)\mathbf{e}_q(Lm1q|JM) \tag{20}$$

In (20) the Clebsch–Gordon coefficients are with the phase convention of of Gordon and Shortley and m, q and M are, respectively, the z-components of L,1 and J. The (nabla)-gradient of a single particle wave function can be written

$$\nabla(\phi_n Y_{v,m_n}) = \phi_{v+} Y_{v,v+1,m_n} + \phi_{v-} Y_{v,v-1,m_n} \tag{21}$$

where we, for the moment, introduce the convention that a state with quantum number n has orbital angular momentum quantum number noted by the corresponding greek letter v

$$\phi_{v+} = -\sqrt{((v+1)/(2v+1))}(\mathrm{d}/\mathrm{d}r - (v+0)/r)\phi_n \tag{22}$$

$$\phi_{v-} = +\sqrt{((v+0)/(2v+1))}(\mathrm{d}/\mathrm{d}r + (v+1)/r)\phi_n \tag{23}$$

The terms in the current contain the factors

$$Y^*_{\kappa,m_k}\mathbf{Y}_{\iota,\lambda,m_i} = \sum_{JlM} \mathbf{Y}_{J,l,M} X_{JlM} \tag{24}$$

where the factor X is constructed from 6J symbols, which are (for typographical reasons) here replaced by the equivalent U symbols of Jahn.

$$\begin{aligned}X_{JlM} = \sqrt{(2\kappa+1)(2\lambda+1)/4\pi(2l+1)}(-)^{m_k} \\ U(1,\lambda,J,\kappa;\iota,l)(\kappa,-m_k,\iota,m_i|J,M)(\kappa,0,\lambda,0|l,0)\end{aligned} \tag{25}$$

From (24) and (25), determined by the Schrödinger equation above, we get the general expressions for longitudinal and transverse transition current densities

$$F^L_{J+}\mathbf{Y}_{J,J+1,M} + F^L_{J-}\mathbf{Y}_{J,J-1,M} \tag{26}$$

$$F^T_{J+}\mathbf{Y}_{J,J+1,M} + F^T_{J-}\mathbf{Y}_{J,J-1,M} \tag{27}$$

In the above, F^L and F^T are coefficients of the expansion of longitudinal and transverse currents in spherical harmonics as noted in Appendix 2. The sum of all the four last terms should be equivalent to the transition current densities calculated from Eqs. 26 and 27, and since the vector spherical harmonics are orthogonal for different values of all three quantum numbers, the same equivalence must be true for the coefficients F. So, from these equations, we get the desired longitudinal current components.

2.2 Description of electrons–nuclei coupled systems

Next, we should like to include a possible motion of nuclei and hence get a set of coupled equations for electrons and nuclei:

$$\begin{aligned}i\partial\phi_j/\partial t = \left(-\nabla^2_r/2 + v_s[n,n_B](\mathbf{r},t)\right)\phi_j(\mathbf{r},t); \\ [j = 1,\ldots,N]\end{aligned} \tag{28}$$

$$i\partial\psi_{A\alpha}/\partial t = \left(-1/(2M_A)\nabla^2_R + V^A_s[n,n_B](\mathbf{R},t)\right)\psi_{A\alpha}(\mathbf{R},t) \tag{29}$$

with nuclear densities

$$n_A(\mathbf{R},t) = \sum_{\alpha=1}^{N_A} n_{A,\alpha}(\mathbf{R},t) = \sum |\psi_{A\alpha}(\mathbf{R},t)|^2 \tag{30}$$

and electron densities

$$n(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2 \tag{31}$$

For more details, see [13].

The important case of $e_i = e_k$ deserves special attention. Here $\mathrm{div}\mathbf{j}_{ki}/e_{ki}$ can be considered a limiting case of $e_k = e_i + d$ for $d \to 0$:

$$(\nabla(\psi_k^*\nabla\psi_i - \psi_i\nabla\psi_k^*))/e_{ki} \tag{32}$$

$$((\Delta\psi_i)\psi_k^* - (\Delta\psi_k^*)\psi_i)/e_{ki} \tag{33}$$

$$bd\psi_i\psi_k^*/e_{ki} = b|\psi_i(r)|^2 \tag{34}$$

The last formulation assumes that we further have $\psi_i = \psi_k$, as in the non-degenerate case of a single particle n, again neglecting the spin. Here b in atomic units is 1.

Different currents

$$\mathbf{j} = \langle\psi(t)|\hat{j}|\psi(t)\rangle \tag{35}$$

and

$$\mathbf{j}' = \langle\psi(t)'|\hat{j}|\psi(t)'\rangle \tag{36}$$

correspond to different external potentials v, v' and therefore to different solutions of KS equations.

Once the external potentials are fixed, all other matrix elements of one- and two-body operators between different states of the system, determined by $\hat{H}$, are given.

From Ehrenfests theorem, applied to the nuclear KS equation, the classical trajectory is given as:

$$\mathbf{R}_{A\alpha}^{\text{class}} = \langle\psi_{A\alpha}(t)|\hat{\mathbf{R}}|\psi_{A\alpha}(t)\rangle \tag{37}$$

$$\int d^3R\mathbf{R}n_{A\alpha}(\mathbf{R},t) \tag{38}$$

We see that

$$M_A d^2\mathbf{R}_{A\alpha}^{\text{class}}/dt^2(t) = \mathbf{F}_{A\alpha}(t) \tag{39}$$

with

$$\mathbf{F}_{A\alpha}(t) = -\langle\psi_{A\alpha}(t)|\nabla_R V_s^A|\psi_{A\alpha}(t)\rangle \tag{40}$$

In some cases, the nuclear densities may be rather narrow distributions peaked around a classical trajectory. Such distributions may, e.g., be forced upon a system by introducing appropriate screening in an experiment. The practical difficulties of such a procedure should not prevent us from using it in a theoretical description, since the spreading of wave-packets in many cases is shown to be *relatively* small (as exemplified by scattering of slow nuclei in Coulomb fields). Under such circumstances the equations of motions for the nuclei reduce to

$$\begin{aligned} &M_A d^2/dt^2\mathbf{R}_{A\alpha}^{\text{class}}(t) \\ &= -\nabla\left[V_{\text{ext}}^A(\mathbf{R}_{A\alpha}^{\text{class}},t) - \int d^3rZ_An(\mathbf{r},t)/|\mathbf{R}_{A\alpha}^{\text{class}} - \mathbf{r}| \right.\\ &\quad\left. + \sum_{B=1}^{K}\sum_{\beta-1}^{N_B} Z_AZ_B/|\mathbf{R}_{A\alpha}^{\text{class}} - \mathbf{R}_{B\beta}^{\text{class}}|\right] \end{aligned} \tag{41}$$

and the electronic KS equations simplify to

$$\begin{aligned} i\partial\phi_j(\mathbf{r},t)/\partial t = &\left[-\nabla^2/2 + v_{\text{ext}}(\mathbf{r},t) + \int d^3r'n(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|\right.\\ &\left.-\sum_{B=1}^{K}\sum_{\beta=1}^{N_B} Z_B\,|\,\mathbf{R}_{B\beta}^{\text{class}}(t) - \mathbf{r}\,|^{-1} + v_{xc}[n,\mathbf{R}_{B\beta}^{\text{class}}(t)](\mathbf{r},t)\right]\phi_j(\mathbf{r},t) \end{aligned} \tag{42}$$

Equations (41) and (42) are evidently coupled, and they must be solved simultaneously, thus achieving the trajectory. In Appendix 5 we have derived the similar equations for the relativistic case thus including the magnetic component of the transition, see Appendix 2.

3 Expressions for time-evolution of electronic states

In the last sections, we introduced the transition currents for calculation of electric and magnetic matrix elements. The advantages of introducing that, as suggested here, are several.

First, these procedures, are known to lead to similar simplifications compared to Hartree–Fock methods as those of density methods [1, 2]. Secondly, the currents give a simpler connection to dynamical problems, than do static densities. Thirdly, we have just shown, that even magnetic interactions can, by means of the currents, be expressed in a particularly simple way. And fourthly, as already shown in [13], special methods for calculations of integrations in matrix elements, permit us to avoid unwieldy, sometimes even singular, integrals.

As a fifth point, it should be mentioned, that the classification used here, of dividing vector functions in longitudinal and transverse vector functions, is a very natural one, when thinking of local, as distinguished from global classifications.

Further simplifications may be obtained by using a special representation for the wave functions, and consequently also for the currents. We shall here, neglecting spin, use the basis of wave functions of electrons around a point nucleus of infinite mass, and charge eZ, factorizing the wave function in the usual way:

$$\phi = 1/r\chi_l(r)Y_{lm}(\theta,\phi) \tag{43}$$

$$\chi_l'' + (-\gamma^2 + 2\gamma\kappa/r - l(l+1)/r^2)\chi_l = 0 \tag{44}$$

$$2mE/\hbar^2 = -\gamma^2 \tag{45}$$

$$\kappa = Ze^2m/(\hbar^2\gamma) \tag{46}$$

(E being the total energy) and introduce a dimensionless radial variable

$$z = r/\alpha_0 = r\gamma = rZ/n \tag{47}$$

Now according to [13] (see also Appendix 2, Eq. 116) the transition current density in this representation has matrix elements given by vector spherical harmonics, cfr. Eqs. 20–27.

$$[\mathbf{j}_{ki}]_{JlM} = [\phi(r)_k Y^*_{l_k m_k} \nabla(\phi(r)_i Y_{l_i m_i}]_{JlM} - [\phi(r) - iY_{l_i m_i} \nabla(\phi(r)_k Y^*_{l_k m_k}]_{JlM} \tag{48}$$

The radial part of $\mathbf{j}_{ki}$ see below in Eq. 51 can be written

$$F_{\alpha,J,l,M} = F^{\alpha}_{J,I,M} - F^{\alpha'}_{J,L,M} \tag{49}$$

$$F^{\alpha}_{J,l,M} = \phi_k \phi_{\imath+} X^{\alpha,\lambda=\imath+1}_{J,I,M} + \phi_k \phi_{\imath-} X^{\alpha,\lambda=\imath-1}_{J,L,M} \tag{50}$$

and similarly for $F^{\alpha'}_{J,L,M}$.

Here α' means that, in the second term of **J** in Eq. 48, the meaning of i,k are interchanged, although ϕ_k still occurs with complex conjugation cfr. [13]. Thus $\alpha = i, j\imath, \kappa i_n, k_n$. See Eqs. 121 and 122 in Appendix 4.

Next, we equate the coefficients of $\mathbf{Y}_{J,l,M}$ in the transition current densities

$$\mathbf{j} = \sum_{J,l=J\pm 1,M} F_{\alpha,J,l} \mathbf{Y}_{J,l,M} \tag{51}$$

and those in $\mathbf{L}_{JM} + \mathbf{T}_{JM}$ we get

$$(\mathrm{d}/\mathrm{d}r - J/r)u_J = F_{\alpha,J,J+1} \tag{52}$$

$$(\mathrm{d}/\mathrm{d}r + (J+1)/r)v_J = F_{\alpha,J,J-1} \tag{53}$$

where

$$u(r)_J = \sqrt{J/(2J+1)}\Phi^T_J - \sqrt{(J+1)/(2J+1)}\Phi^L_J \tag{54}$$

$$v(r)_J = \sqrt{J/(2J+1)}\Phi^L_J + \sqrt{(J+1)/(2J+1)}\Phi^T_J \tag{55}$$

The differential Eqs. 52 and 53 are to be solved to get $u(r)$, $v(r)$. Although this is not difficult for small molecules, in the case of larger molecules it could be time consuming. An alternative method could be to expand the $F_{\alpha,J,l}$ on functions which lead to algebraic solutions of Eqs. 54 and 55 as would be the case if the transition currents were currents in atoms with a fixed nucleus of point charge. Regardless of how the above equations are solved, the next step should be to invert the equations to get the $\boldsymbol{\Phi}^L_J, \boldsymbol{\Phi}^T_J$ from which the electric, respectively magnetic electron interactions are constructed (see Appendix 4)

$$\Phi^L_J = v_J\sqrt{J/(2J+1)} - u_J\sqrt{(J+1)/(2J+1)} \tag{56}$$

$$\Phi^T_J = u_J\sqrt{J/(2J+1)} + v_J\sqrt{(J+1)/(2J+1)} \tag{57}$$

These equations constitute the main framework for solving the evolution of the electronic structure in molecules. The equations are in time, meaning that the parameter, or the argument, of the two electron evolution equations can be considered as any variable since the potentials, and therefore also the F's, are time-dependent. The time-dependence is basically through the nuclear dynamics, see Sect. 2.2. Ehrenfest theorem of the time evolution of the wave-packet can also be applied in this case guaranteeing that the time evolution of $u(r, t)$, $v(r,t)$ will have an extra time parameter in the exponent. Such parameter, however, disappears in the calculation of the density and the density of the currents. Overall, we build the formalism for the transition currents between different orbitals in time. Thus we can write:

$$u(r,t)_J = \sqrt{J/(2J+1)}\Phi(r,t)^T_J - \sqrt{(J+1)/(2J+1)}\Phi^L_J(r,t) \tag{58}$$

$$v(r,t)_J = \sqrt{J/(2J+1)}\Phi(r,t)^L_J + \sqrt{(J+1)/(2J+1)}\Phi^T_J(r,t) \tag{59}$$

and similarly for $\Phi(r,t)$:

Equations (52) and (53), and the ones just mentioned, are of the linear type, which are described and, generally, solved in standard text books, e.g., Kamke [14]. With the notation given in Ref. [14], both equations can be written as:

$$\mathrm{d}y/\mathrm{d}x + f(x)y = g_y(x) \tag{60}$$

with the solution:

$$y = \exp(-F)[a + \int_b^x g(x')\exp(F)\mathrm{d}x'] \tag{61}$$

We could also have started from the equation:

$$\mathrm{d}y/\mathrm{d}x + A/xy = g^{A(x)} \tag{62}$$

that has the solution

$$y = x^{-A}\int_{x_0}^{x} x'^A g^A(x')\mathrm{d}x' \tag{63}$$

where $g^A = F_{\alpha,J,J+1}(x)$ for $A = -J$ and similarly $g^A = F_{\alpha,J,J-1}(x)$ for $A = J+1$.

The field functions, F, that appeared above and in y, are given by:

$$F(x)^u = F(r) = -\int_b^r \frac{(J+1)}{r'}\mathrm{d}r' = r^{-J}/b^{-J} \tag{64}$$

whereas in the next equation

$$F(x)^v = \int_b^r \frac{(J)}{r'}\mathrm{d}r' = r^{-J+1}/b^{-J+1} \tag{65}$$

The lower limit of the two integrals are close to zero. Next, we will write

$$g_u(r) = \exp(-\gamma r)G_u(r) \tag{66}$$

$$g_v(r) = \exp(-\gamma r)G_v(r) \tag{67}$$

and expanding the G-functions in a Taylor series around $r = 0$. Hence

$$G_u = \sum_{n=0}^{N} A_n^u r^n; \quad G_v = \sum_{n=0}^{N} A_n^v r^n \tag{68}$$

The equation for $v_J(r)$ has the solution

$$v_J = r^{-(J+1)} \int_0^r \mathrm{d}r' r'^{(J+1)} F^v_{\alpha,J,J-1}(r') \tag{69}$$

and correspondingly for u_J but with $A = -J$:

$$u_J = r^{-(J)} \int_0^r \mathrm{d}r' r'^{(J)} F^v_{\alpha,J,J+1}(r') \tag{70}$$

which we may solve in a similar way, assuming that J is different from 1. (The case, $J = 1$, can be dealt with by a limiting procedure, $J \rightarrow 1$). All together we get for the first term. e.g., in the Taylor expansion of F:

$$A_1^{\text{Taylor}} = F_0(r^J r^{-(J+1)} - b^J b^{-(J+1)}); \quad b \rightarrow 0 \tag{71}$$

We see, that the electron–electron interaction strength, corresponding to the two transitions:

$$\alpha = [i, k] \tag{72}$$

$$\beta = [j, h] \tag{73}$$

is given directly by the scalar product of the corresponding transition current densities, integrated over all space. Antisymmetry of the wave functions simply means that the Pauli exclusion principle should be implemented on each pair of states. In [13], another way of writing j^L_{ki} was suggested, see Eq. 7:

$$j(r)^L_{ki} = \int \mathrm{d}r'^3 \nabla_{r'}(\rho(r)_{ki} i E_{ki}/(4\pi\hbar \mid r \mid) \tag{74}$$

We see, that with this formulation, inconvenient energy denominators E_{ki} are removed.

The transition matrix element from one orbital Ψ_0 to another Ψ_1 is described by

$$\langle \Psi_0 | \, \hat{\mathbf{j}}(r) | \, \Psi_1 \rangle$$

where the transition current $\mathbf{j}$ is given by Eq. 48 with Eqs. 51–56 or in Appendix 5.

For molecules a somewhat similar method is described in Sect. 4 of this paper. In general, the simplifications obtained by our method as given by Eqs. 11–16 are evident when the wave-functions, say for one atom, are connected by raising and lowering operators for l as well as for the radial number n, see Refs. [15–17], which form a complete system. This can be used for expansion of the total wave-function.

4 Molecular calculations

In this section, we shall show how one, instead of the spherical harmonics, can make use of Gaussian wave functions since they are the standard tools in the usual DFT programs that we wish to compare our theory with.

We shall first show some general tools for molecular calculations before going to analyze specific molecules. Basically, we are interested in a proof of the completeness of the current formalism of DFT.

When treating molecules we shall first look at one electron interacting with several nuclei. Later we shall look at the repulsion between electrons. Since the mass of nucleons is much larger than that of electrons, we shall describe the motion of nuclei classically and also neglect internal excitations corresponding to nuclear dynamics j, h above, so we look at an electronic excitation from the level i with quantum numbers n, m, l ad write the wave function

$$\chi_{nlm}(\mathbf{r} + \mathbf{R}) \tag{75}$$

connected with a nucleus at $\mathbf{R}$. It is by the nuclear Coulomb attraction moved to an orbit with quantum numbers n', m', l' round a nucleus at the origin. The Coulomb transition matrix element is:

$$\int \mathrm{d}^3 r \chi_{n'm'l'}(\mathbf{r})^* \mathbf{Z}/\mathbf{r} \chi_{\mathbf{nml}}(\mathbf{r} + \mathbf{R}) \tag{76}$$

In the formulation of Shibuya and Wulfman [15], this amplitude of exciting a state k from a transported χ_i is denoted

$$\int \mathrm{d}^3 r \chi_i(\mathbf{r} + \mathbf{R}) = \sum_{\mathbf{j}} \chi_{\mathbf{i}}(\mathbf{r}) \mathbf{S}(\mathbf{R})^{\mathbf{j}}_{\mathbf{i}} \tag{77}$$

where, in agreement with the above,

$$S^j_i = \int \mathrm{d}^3 r \chi_i(\mathbf{r})^* \mathbf{Z}/\mathbf{r} \chi_{\mathbf{j}}(\mathbf{r} + \mathbf{R})/\mathbf{k^2} \tag{78}$$

and where the last factor is due to normalization.

The interaction matrix between one electron with transition density $\rho(\mathbf{r})_{\tau'\tau}$ and several nuclei densities, $\rho(\mathbf{X_a})_{\mathbf{T'T}}$ is

$$S_{\tau'\tau} = \sum_a \int \rho_{\tau'\tau} \mathrm{d}^{3r} 1/|r - X| \int \rho_{T'T}$$

We here follow Ref. [17] and let τ denote the centre of the position of the electron density (of course $=X_a$) as well as its spherical quantum numbers. From the Schrödinger equation of the electron, as well as its consequence, the continuity of transition time-dependent transition densities we arrive at the expression for $S_{\tau'\tau}$

$$S_{\tau'\tau} = \int_j L_{\tau'} J_{T'T} \hbar^2 4\pi \mathrm{d}^3 r/(E_{\tau'\tau} E_{T'T})$$

where L stands for the longitudinal component of the transition probability. Since the nuclei are so much heavier than the electrons we may approximate $J_{T'T}$ with a classical density of point charges, whereas $j^L_{\tau'\tau}$ is still the quantum density of longitudinal currents. Now, the $S_{\tau'\tau}$ obviously forms a representation of the group of translations based on Sturmian bound state densities, e.g., as used by Avery [17].

4.1 Gaussian integrals

Next we return to the Gaussian integration tools. This is in order to compare our results with those from DFT that use the computer program-packet Gaussian suite of programs [18]. The Gaussian tools within this packet are used as means for saving computer time since Gaussian integrals converge faster than spherical harmonics ones and Legrendre radial functions. The so-called Gaussian terms are appearing in a power series.

Concerning a Gaussian expansion for the wave functions, it is natural to start from expression (15) where $j(r)$ now is:

$$j(r)^L_{ki} = \mathrm{grad}_r \int \mathrm{d}r'^3 \rho(r')_{ki} iE_{ki}/((r_-)4\pi\hbar) \tag{79}$$

$$[Y_{J,J-1,M} \text{ for } A = J+1] \tag{80}$$

$$[Y_{J,J+1,M} \text{ for } A = -J] \tag{81}$$

Each Gaussian term (being of the form $\int \mathrm{e}^{-\lambda x^2} x^k \mathrm{d}x$ now get a radial form

$$w(r) = r^{-A} \int_0^r \mathrm{d}r' r' A \rho(r') C \tag{82}$$

where $A = J + 1$ when the vector spherical harmonics is $Y_{J,J-1,M}$ but $A = -J$ for $Y_{J,J+1,M}$. The argument from [13], that (107) will lead to finite integrals, independently of the sign of A, is still valid as noted in connection with Eq. 105. Let us look at one term in a Gaussian expansion of an ordinary electron density

$$j(r)^L_{kk}/E_{kk} = \int \mathrm{d}r'^3 \mathrm{grad}_{r'} \rho(r')_{kk} i/(4\pi\hbar |r_{|}) \tag{83}$$

Considering one term in a Gaussian expansion of an electron density (an ordinary, non-transition density) $\rho(\mathbf{r})_{kk}$, we can use the above formula to get

$$\begin{aligned} \mathrm{grad}_r[\rho(r)] &= \mathrm{grad}_r(F(r)Y_{JM}) \\ &= -\sqrt{(J+1)/(2J+1)}(\mathrm{d}/\mathrm{d}r - J/r)F(r) \\ &\quad \times Y_{J,J+1,M} + \sqrt{J/(2J+1)} \\ &\quad \times (\mathrm{d}/\mathrm{d}r + (J+1)/r)F(r)Y_{J,J-1,M} \end{aligned} \tag{84}$$

The two terms correspond to $A = -J$, respectively $A = J + 1$. Next, we have:

$$F(r) = \mathrm{e}^{-\beta r^2} \tag{85}$$

where each radial differential equation has the solution

$$r^A \int \mathrm{d}r'(r')^{-A} F(r') \tag{86}$$

When the F's are error functions the integrals are given by

$$\int_{-\infty}^{0} (r')^A \mathrm{e}^{-\beta(r')^2} = 1/2(-1)^A(\beta)^{(-1-A)/2}\Gamma[(1+A)/2] \tag{87}$$

$$\begin{aligned} \int_0^r (r')^A \mathrm{e}^{-\beta(r')^2} &= 1/2 r^{1+A}(r^2\beta)^{1/2(-1-A)}(\Gamma[(1+A)/2] \\ &\quad - \Gamma[(1+A)/2, r^2\beta)]) \end{aligned} \tag{88}$$

The Gaussian densities, with their short ranges, are of course not very well fit for calculation of the effects of the long range Coulomb interactions, but since they are easy to calculate, they are widely used.

4.2 The case of the ZnO and water molecules

As an example of the use of the suggested method, we shall look at the molecule of ZnO. It plays an important role in many organic compounds. We shall here, as suggested in [13] use elliptic coordinates, which separate the kinetic energy operator, and also the potential energy of one electron in the Coulomb potential from nuclei at rest. Therefore, it can be written in the form

$$V = (V_I(r_1 + r_2) + V_{II}(r_1 - r_2))/r_1 r_2 (+V(\phi \ldots)) \tag{89}$$

Here r_1 and r_2 are the distances of the electron to nucleus-1 and nucleus-2, respectively and ϕ the angle of the position of the electron around an axis trough both nuclei. The standard elliptical coordinates are now ϕ and

$$\xi = (r_1 + r_2)/R \tag{90}$$

$$\eta = (r_1 - r_2)/R \tag{91}$$

Here R is the distance between the two nuclei. To get simple formulae, we chose units so that this distance is 2. The components of the gradient of the electron transition density are now

$$[\mathrm{grad}_\phi, \mathrm{grad}_\xi, \mathrm{grad}_\eta]\rho \tag{92}$$

which we shall list below in the order:

$$\sqrt{(1-\cos^2\phi)/((\xi^2-1)(1-\eta^2))}\partial\rho_{ki}/\partial\phi \tag{93}$$

$$\sqrt{(\xi^2-1)/(\xi^2-\eta^2)}\partial(\rho_{ki})/\partial\xi \tag{94}$$

$$\sqrt{(1-\eta^2)/(\xi^2-\eta^2)}\partial(\rho_{ki})/\partial\eta \tag{95}$$

Omitting again the spin, the solution of the one electron Schrödinger equation in elliptical coordinates has the form

$$\psi_{k,|m|}(\xi,\eta)\mathrm{e}^{\mathrm{i}m\phi} = \sum_{n=0,l=|m|} c^{k}_{n,l,|m|}\mathrm{e}^{\mathrm{i}m\phi}P_l^{|m|}(\eta)F_{k,n,|m|}(\xi) \tag{96}$$

Here the solutions in terms of the η, ϕ coordinates are well known and simple, whereas the F functions in terms of ξ are only known in special cases. They are nevertheless easy to find from the separated Schrödinger equation in elliptical coordinates. As a rough approximation we may take the number of relevant states as being the same as the number of Gaussian states in the single particle atomic orbital approximation, i.e., with spin 54 basis functions. In the atomic orbital approximation, 22 of these are concentrated around O, the other 32 are concentrated around Zn. Overall, we see that it is possible to get an understanding of the occupation probability by taking the square of the equation above, which mainly mount to taking the square of $F_{k,n,|m|}$.

Although H_2O is again an inorganic molecule, it also plays a large role in many organic compounds and reactions. It is interesting as an example of a more complicated use of the suggested method

$$\chi(H_2O) = A\chi_1(H)\chi_2(H)\chi(O) \tag{97}$$

Here A is an anti-symmetrizing operator on the electron wave functions. It is not so important, because the electron wave functions for different atoms in a molecule have rather small overlaps. We treat the nuclei in a classical approximation. Now, the hydrogen electron wave functions are Shibuya–Wulfman integral factors [15, 17] translated to the centre of the oxygen atom

$$\chi_{i,v}(\mathbf{x}+\mathbf{R_i}) = \sum_{v'}\chi_{v'}(\mathbf{x})S^{v}_{v'}(\mathbf{R_i}) \tag{98}$$

Hence the product of the two hydrogen functions in (137) becomes

$$A\chi_{1,v}(\mathbf{x})\chi_{2,v'}(\mathbf{x})\sum_{v''}S^{v''}_{v'}(\mathbf{R_1})S^{v}_{v''}(\mathbf{R_2}) \tag{99}$$

Due to the group properties of the Shibuya–Wulfman factors, the last sum of products of these can be written as

$$\sum_{v''}S^{v''}_{v'}(\mathbf{R_1})S^{v}_{v''}(\mathbf{R_2}) = S^{v}_{v'}(\mathbf{R_1}+\mathbf{R_2}) \tag{100}$$

Although this expression looks a little complicated, it must be remembered, that the Shibuya–Wulfman integral factors afford an extremely useful tool in any molecular calculation. The square of the factor $S^{v''}_{v'}(\mathbf{R_1})$ is a transition probability between v and v' states. Programs for their calculation at different values of $\mathbf{R_{ij}}$ are or ought to be available in a near future at centers of such calculations, thus solving one main problem of these calculations: the interaction between electrons and nuclei for different configurations. The other main problem: the interaction between electrons, may then be solved by the methods suggested here or by some modifications of those.

In [13] one method of describing the Coulomb interaction between electrons in atoms and molecules was given. Here we shall suggest a similar method for the interactions between electrons and nuclei. We start from Eq. 4 of [13]. Let the q.n.s of an electron orbital around a nucleus (charge Z) at $\mathbf{R}$ be nlm. In the following, we suppress lm and denote the orbital $\chi_n(\mathbf{r}+\mathbf{R})$ and an (excited) orbital $\chi_{n''}$. Similarly we denote the states of the nucleus $\chi_{N'}, \chi_{N''}$. As in [13] the general Coulomb matrix element is

$$C\int \mathrm{d}r^3\int \mathrm{d}r'^3\mathrm{div}j_{n''n}\mathrm{div}j_{N''N'}/|r-r'| \tag{101}$$

but since r' is now the coordinate of a nucleus, we may assume, that its deviation from 0 is negligible, and just write a classical approximation (also neglecting its internal excitations)

$$j_{N''N''} = C_N\delta(r')$$

We then get the amplitude for exciting the electron from an orbital χ_n around $\mathbf{R}$ to another orbital $\chi_{n''}$ around 0 by means of the Coulomb field from a nucleus at 0:

$$C\int \mathrm{d}r^3\chi^*_{n''}(bfr)Z/r\chi_n(\mathbf{r}+\mathbf{R}) \tag{102}$$

Note, that the relations between transition charge densities and transition current densities are general and do not depend on whether the normalization is Schrödinger or Sturmian, or on the orthogonality of $\chi_n, \chi_{n''}$; not even on whether the argument of the χ is $\mathbf{r}$ or $\mathbf{r}+\mathbf{R}$. Introducing C above as the reciprocal of the double kinetic energy of electrons (common to all Sturmian states) we get our amplitude equal to the $S^{n}_{n''}(\mathbf{R})$ introduced by Shibuya and Wulfman in their important work on molecular electronic wave functions. Using Sturmian states also for the complete molecular wave function we then come to the same secular equation as these authors:

$$\sum_{\tau}\left[v_{\tau'\tau} - k_\mu S_{\tau'\tau}\right]C_{\tau\mu} = 0 \tag{103}$$

Here the index τ includes both the quantum numbers nlm and also an index describing the position of the various nuclei of the molecule; the v matrix represents the interaction between one electron and the totality of nuclei of the molecule. The solution of this secular equation thus gives the motion of one electron To solve the total molecular problem one should then include the effect of electron–electron interaction, which is the main theme of this paper, and add the classical description of the motion of nuclei, including their repulsion from each other, all three steps might be repeated to convergence.

In the Shibuya–Wulfman paper, Ref. [15], much work is connected to the introduction of a momentum space representation of electron wave functions. Nevertheless, the final expression for their S is written in position space, like here.

At the end it is important to address the issue of gauge invariance when including magnetic fields. Basically, the original current theory contains quantities being gauge dependent. However, all the physical quantities, the observables, are operators whose expectation values are gauge invariant. On the other hand the current is gauge dependent and making use of the current requires solutions to this problem. Some of the analytical solutions, Refs. [11, 19], involve the inclusion of a particular form of exchange-correlation.

There are, however, another gauge symmetry, the one connected to the origin dependence and that has been carefully discussed also in Refs. [11, 19], the problem is when getting observables through an optimization based on a truncated basis set. In our case the large set of spherical harmonics will save the origin gauge symmetry [20].

5 Numerical treatments

In the following, we present some analysis on how to employ the present methods to molecular systems. This will make use of some of the modern computer software for deriving physical properties of molecules on the basis of their crystallographic databases. Many of the algorithms for these tasks are embedded in the molecular dynamics program packages.

Let us here briefly describe one of such procedures we have in mind, by giving the following example of a large molecular system. An example that illustrates the importance and usefulness of solving our equations of the time-development of the electronic systems are zinc molecules or molecules where zinc atoms are incorporated. We have especially the proteins that contain copper ligands of which one medium size protein is alcohol dehydrogenase.

The first step is, as for any molecular dynamics simulation that does not start from ab initio configurations, to obtain the full set of atomic cartesian coordinates representing the initial configuration. This set of coordinates is obtained from the X-ray crystallographic databank. One might ask if that is necessary for a quantum mechanical calculation but an initial molecular dynamics energy minimization is always required for positioning surrounding solvent molecules such as water and other ligands and this classical molecular dynamics is also in our case necessary before solving for quantum time trajectories.

Once this initial molecular dynamics equilibration is performed we can ask for electrostatic configuration that next should be the input to our electronic time-dependent equations. We wish to have the field strength tensor constructed and that is done, either from a multi-pole expansion or directly from the force field where fields are obtained from the nablaient (differential napla operator) of the energy potentials build up from the atomic coordinated, the bond lengths and the bond angles.

5.1 Comparison of the standard DFT's and our method's numerics

In the following subsection, we shall describe how one can assess the various numerical treatments of the molecules mentioned above. We shall, within these examples, compare the numbers about electronic orbitals calculated with the help of usual theoretical DFT techniques and techniques based on our electronic wave equations [7]. The applications are very restricted in the sense that only ground states are considered. In a forthcoming study transitions to excited states are considered. However, excited states in molecules need further clarification, such as Homo-Lumo states in terms of atomic orbitals.

We give the results from a DFT calculation of the small molecules using the Gaussian program from where we have listed all the occupation probabilities of the available quantum states. Thus we can then employ the formulas derived above to derive the occupation numbers from our method.

The first case we have studied numerically is the zinc-oxide molecule. In Table 1, we have listed the occupation probabilities of the electrons in the various ground states.

Table 1 A comparison of the different calculations of occupation probabilities (Mulliken) in atomic orbitals (AO) of oxygen in various simple molecules

Molecule type (MD)	AO 2s (DFT)	AO px (DFT)	AO py (DFT)	AO 2s (BB)	AO px (BB)	AO py (BB)
ZnO	1.02/0.95	0.65/0.43	1.03/0.74	1.05/0.98	0.62/0.41	1.01/0.72
$4H_2O$	0.90/0.91	1.00/0.71	0.97/0.69	0.94/0.95	0.97/0.69	0.94/0.67

The two methods that are compared are the standard DFT calculation with Gaussian error functions and our method BB presented by spherical harmonics. The population is according to Mulliken-prescription, i.e., core contribution minus valence. The p-orbitals are described by the coordinates x, y and z. The py and pz occupation is the same. In the case of water four molecules are taken together forming a tetrahedra bound together by H-bonds. Both spin-states are listed as s_1/s_2

As is seen from the table there is reasonable agreement of the stationary population statistics in the lower atomic orbitals of the two methods. Our method is supposed to be superior with respect to excited states dynamics, the transition amplitudes and other time-dependent quantities. However, it is hard to find other numbers to use for comparison other than the stationary population dynamics.

5.2 Conclusion

A quantum mechanical formalism for atoms and molecules have been proposed based on currents rather than densities and which are decomposed into transversal and longitudinal components. In order to give a complete dynamical description of the currents, magnetic fields have been included and thus, necessarily, relativistic effects. This formalism is aspiring at calculating transition probabilities between different states which, in principle, is possible within this formalism and in a molecular frame-work. However, the examples of numerical treatments given here are just static cases of two very simple molecules in the ground state for which the occupancies are estimated. The wave functions in this formalism are expanded on spherical harmonics but we also employ the more useful Gaussian integrals into which the wave functions are expanded as in the usual numerical DFT treatments [3].

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Appendix 1: An expression for an exchange-correlation energy

Let us briefly mention an earlier derivation of an exchange-correlation expressed as a difference, $Q = V - V_H$ between the total potential V and the Hartree potential, V_H, and with the help of a new central potential term, also used by Talman and Shadwick, see Ref. [13], as well as in Eqs. 11–16. We may then write:

$$Q = \sum_i \sum_{j \neq i} \int \mathrm{d}\mathbf{r}'^3 \int \mathrm{d}\mathbf{r}''^3 \frac{\psi_i(\mathbf{r})^* \psi_k(\mathbf{r}')}{E_i - E_j} 2 \times \sum_k \frac{\psi_j(r)^* \psi_k(\mathbf{r}') \psi_k(\mathbf{r}'')^* \psi_i(\mathbf{r}'')}{\mid \mathbf{r}' - \mathbf{r}'' \mid} \tag{104}$$

which can be simplified using the same restriction on the indices of Coulomb matrix elements, as in Ref. [2]:

$$Q = C \sum_i \sum_{j \neq i} \frac{\psi_i(\mathbf{r})^* \psi_k(\mathbf{r}')}{E_i - E_j} \int \mathrm{d}r' \frac{(\mathbf{j}^L_{jk}(\mathbf{r}') \mathbf{j}^L_{kl}(\mathbf{r}'))}{(E_k - E_i)(E_j - E_k)} \tag{105}$$

where $C = \hbar 8\pi$. It is quite remarkable that one can obtain such relatively simple expression for the exchange-correlation. This is a contribution between different orbitals or quantum states i, j. In the case of $E_i = E_j$ this term vanishes and we are left with the zero'th order Born term. For details see Ref. [2].

Appendix 2: Transition charge density

For the sake of consistency of the paper this appendix brings a derivation of the expression, following the prescription of Ref. [13] for the transition current densities that are used in Sects. 3 and 4 of the present paper. We start, as in Ref. [13] from an expression for the one-particle transition charge density:

$$\rho(r)_{ki} = e\psi(r)^*_k \psi(r)_i \tag{106}$$

where $\psi(r)_k$, $\psi(r)_i$ are the one-particle energy eigen-states and where the numbers i, k stand for the radial, angular momentum,..., etc. The perturbative matrix element for the residual Coulomb interaction between two electrons situated at r and r' is then expressed by the integral:

$$I_C = \int \mathrm{d}r^3 \int \mathrm{d}r'^3 \frac{\rho(r)_{ki} \rho(r')_{jl}}{|r - r'|} \tag{107}$$

and applying the time-dependent Schrödinger equation for ψ the integral can be written as

$$I_C = -\int \mathrm{d}r^3 \int \mathrm{d}r'^3 \frac{1}{|r - r'|} \frac{\partial \rho(r)_{ki}}{\partial t} \frac{\partial \rho(r')_{jl}}{\partial t} (E_{ki} E_{jl})^{-1} (\hbar)^2 \tag{108}$$

where $E_{ij} = E_i - E_j$. If one again applies the continuity equation of transition charge densities one can write the integral I_C:

$$I_C = -\int \mathrm{d}r^3 \int \mathrm{d}r'^3 \frac{1}{|r - r'|} \mathrm{div}_r \mathbf{j}(\mathbf{r})_{ki} \mathrm{div}_{r'} \mathbf{j}(\mathbf{r}')_{jl} \times (E_{ki} E_{jl})^{-1} (\hbar)^2 \tag{109}$$

with j_{ij} being the transition current:

$$\mathbf{j}_{ij} = a(\psi_i^* \nabla \psi_j - \psi_j \nabla \psi_i^*) \equiv \mathbf{j}^\alpha \mathbf{j}^\beta \tag{110}$$

where $a = \frac{e\hbar}{2mi}$ and where α, β correspond to the quantum numbers of the interchange of the states i,j. One should remark that, fortunately, if the denominator E_{ij} is zero then the numerator is also zero.

We are now in position to derive the very important expressions for the current that are used in Sect. 3. These expressions have been derived with the powerful tool of vector algebra where the vectors, in this case the transition current densities, are split into longitudinal parts, j^L, and transverse parts, j^T as seen below:

$$\mathbf{j}(\mathbf{r})^L = -\mathrm{grad}_r \int \mathrm{d}\mathbf{r}'^3 \mathrm{div}_{r'}\mathbf{j}(\mathbf{r}') \frac{1}{(4\pi \mid \mathbf{r}-\mathbf{r}' \mid)} \tag{111}$$

which in terms of densities is:

$$\mathbf{j}(\mathbf{r})^L_{ij} = \int \mathrm{d}r'^3 \mathrm{grad}_{r'}\rho(\mathbf{r}')_{ij} \frac{iE_{ij}}{(4\pi \mid \mathbf{r}-\mathbf{r}' \mid \hbar)} \tag{112}$$

and

$$\mathbf{j}(\mathbf{r})^T = \mathrm{curl}_{r'} \int \mathrm{d}\mathbf{r}'^3 \mathrm{curl}_{r'}\mathbf{j}(\mathbf{r}') \frac{1}{(4\pi \mid \mathbf{r}-\mathbf{r}' \mid)} \tag{113}$$

which altogether can be written as $\mathbf{j} = \mathbf{j}^L + \mathbf{j}^T$.

With these expressions inserted in Eq. 146 and subsequently performing a partial integrations one finally obtain:

$$I_C = \frac{\hbar^2 4\pi}{E_{ij}E_{kl}} \int \mathrm{d}\mathbf{r}^3 \mathbf{j}(\mathbf{r})^L_{ki} \mathbf{j}(\mathbf{r})^L_{jl} \equiv \frac{\hbar^2 4\pi I^L}{E_{ij}E_{kl}} \tag{114}$$

which therefore transform the sixth-dimensional integral at the start of the appendix to a much simpler three-dimensional integral of the scalar product of the two transition current densities. There are similar expressions valid for the transverse component. However, only the longitudinal ones are used for the calculation of the Coulomb matrix elements.

Appendix 3: Relativistic electrons

Another interesting problem is connected with relativistic effects. The kinetic energies of electrons in atoms and molecules are only in the neighbourhood of the very heaviest nuclei of such an order of magnitude that relativistic effects come into play in a direct way. However, magnetic interactions can always be considered as relativistic effects, and a proper treatment as that may be, not only consistent, but also the simplest way, as shown below.

The electric current density in the Dirac theory of relativistic electrons is given as the 3-vector part of a 4-vector:

$$s_{v=1,2,3,4} = iec\mathbf{\Psi}\gamma_v\mathbf{\Psi} \tag{115}$$

$$s_{k=1,2,3} = j_k; \ldots s_4 = ic\rho \tag{116}$$

The 4-vector s_v can be decomposed

$$s_v = s_v^C + s_v^P \tag{117}$$

so that the space part of s^C, the *conduction current* is of the same form as the non-relativistic expression for j_k. The remaining part is the *polarization current* ${s^P}_k$. The Dirac State vector is here

$$\mathbf{\Psi} = \sum_v \psi_v \mathbf{e}_v \tag{118}$$

and the conjugate

$$\mathbf{\Psi} = \mathbf{\Psi}^\dagger\alpha_0 = \sum_v \bar{\psi}_v \mathbf{e}_v^T \tag{119}$$

where $\mathbf{e}_v^T$ stands for the transposed of $\mathbf{e}_v$.

Here the ψ are functions of x, y, z, t and the $\mathbf{e}$ are orthogonal unit vectors in spin space. The Dirac equation is now

$$\begin{aligned}&\left[\alpha_0 mc + \sum_k \alpha_k\left(\frac{\hbar}{i}\frac{\partial}{\partial x_k} - \frac{e}{c}A_k\right) + e\phi\right]\mathbf{\Psi}\\ &= \left[\alpha_0 mc\mathbf{\Psi} + \alpha\cdot\left(\frac{\hbar}{i}\nabla\mathbf{\Psi} - \frac{e}{c}\mathbf{A}\mathbf{\Psi}\right) + e\phi\mathbf{\Psi}\right] = -\frac{\hbar}{ic}\frac{\partial\mathbf{\Psi}}{\partial t}\end{aligned} \tag{120}$$

Here α is a vector with components α_k and $\alpha_0 = \rho_0$, the familiar Dirac matrices. The continuity equation in this relativistic case becomes

$$\frac{\partial(\mathbf{\Psi}^\dagger\mathbf{\Psi})}{\partial t} = -c\ \mathrm{div}(\mathbf{\Psi}^\dagger\alpha\mathbf{\Psi}) \tag{121}$$

Any field in three-dimensions may be split in a longitudinal and a transverse part

$$\mathbf{j} = \mathbf{j}^{\mathrm{long}} + \mathbf{j}^{\mathrm{tran}} \tag{122}$$

$$\mathbf{j}^{\mathrm{long}} = -\nabla_r \int \mathrm{d}^3 r' \frac{\mathrm{div}_{r'}\mathbf{j}(\mathrm{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|} \tag{123}$$

Let the transition current field be given by its relativistic form in spherical coordinates

$$\mathbf{j}^1_{ki} = iec\bar{\mathbf{\Psi}}_k\gamma\mathbf{\Psi}_i \tag{124}$$

with the spinors

$$\mathbf{\Psi}_{i,J_i,l_i,M_i} = \mathcal{F}(r,t)_i\mathcal{Y}_{lm}\chi_\mu\left(lm\frac{1}{2}\mu|JM\right). \tag{125}$$

In the presence of a magnetic field, the one electron current density takes the form

$$\mathbf{j}^{\mathbf{A}}_{ki} = \frac{\hbar}{2mi}\left(\mathbf{\Psi}^*_k\nabla\mathbf{\Psi}_i - \mathbf{\Psi}_i\nabla\mathbf{\Psi}^*_k - \frac{2ie}{c\hbar}\mathbf{A}\mathbf{\Psi}^*_k\mathbf{\Psi}_{\mathbf{i}}\right) \tag{126}$$

or in spherical form

$$\mathbf{j}^A = C_1\mathbf{j}^1_{JlM} - C_2(\mathbf{A}\rho)_{JlM} \tag{127}$$

where the C's can be derived from equations of the earlier subsections e.g., (45)–(47) and $(\mathbf{A}\rho)_{JlM}$ is given by the definition of vector spherical harmonics in the expression

$$\mathbf{A}\rho = \mathbf{A}\sum_{mq} Y_{lm}\mathbf{e}_q(lm1q|JM) \tag{128}$$

Remember that $\mathbf{A}$ is a vector, ρ a scalar. The *longitudinal* part of these vectors is now found in the same way as in Appendix 2 and in Ref. [13]. In order to treat the magnetic interactions between electrons and between nuclei as well as between nuclei and electrons, we shall look at the transverse transition current densities. At the same time we shall introduce a new form of these current densities, appropriate for the interactions with magnetic fields:

$$\mathbf{s}_{ki} = \mathbf{j}_{ki} - \frac{e^2}{c}\mathbf{A}\boldsymbol{\Psi}_k^*\boldsymbol{\Psi}_i \tag{129}$$

$$\mathbf{s}^T = \mathrm{curl}_r \int \mathrm{d}^3\mathbf{r}' \frac{\mathrm{curl}_{r'}(\mathbf{s}(\mathbf{r}') - \frac{e^2}{c}\mathbf{A}\rho(\mathbf{r}'))}{4\pi|\mathbf{r} - \mathbf{r}'|} \tag{130}$$

with

$$\rho(\mathbf{r}') = \Psi_k^*(\mathbf{r}')\Psi_i(\mathbf{r}') \tag{131}$$

The new expression for the current density gives the same continuity expression as the previous one. The curl **A** = **H** gives the connection to the magnetic field (which could originate from other electrons or nuclei, static or in transitions in general $(j - h)$). The magnetic interaction energy $[ki, jh]$ can again be written by means of the integral of a scalar product of two transition current densities, $\mathbf{j}_{ki}^T$ and $\mathbf{j}_{jl}^T$. Note, however that the two proportionality constants in the electric and magnetic energies, expressed by means of currents, are different. To show the effect of the method of giving the matrix elements by means of currents,we shall start from the final result and work backwards:

$$I_M = \int \mathrm{d}^3r(\mathbf{j}(\mathbf{r})_{ki}^T.\mathbf{j}(\mathbf{r})_{jh}^T)C_{ki,jh} \tag{132}$$

where

$$\mathbf{j}(\mathbf{r})^T = \mathrm{curl}_r \int \mathrm{d}^3\mathbf{r}' \frac{\mathrm{curl}_{\mathbf{r}'}\mathbf{j}(\mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|} \tag{133}$$

(Note, however, that the constant C in the magnetic matrix elements is different from the corresponding constant in the electric matrix element).

Note also, that the current in the magnetic matrix element must include the electromagnetic potential **A**, and that the transverse current densities have the same form as the source terms of *electric* multi-pole radiation (and vice versa with magnetic multi-pole radiation).

The occurrence of curl **j** in the last equation above and elsewhere may seem inconvenient, since this expression is not part of the common formulae, derived from Maxwell's or Schrödinger's equations. Introducing

$$\mathbf{j}^\mathbf{T} = \mathbf{j} - \mathbf{j}^\mathbf{L} \tag{134}$$

this formal problem is avoided.

Appendix 4: Transverse and longitudinal parts of $F_{\alpha,J,\ J}'$

This last appendix will bring a few essential formulas for the vector fields that are used in the present article.

The transverse and longitudinal vector fields are, in the spherical vector representation, defined by the following equations:

$$\mathbf{T}_{J,J,M} = F(r)_{J,J}\mathbf{Y}_{J,J,M}, \text{ with } J \text{ integer } (J > 0) \tag{135}$$

and

$$\mathbf{L}_{J,M} = F(r)_{J+}^L\mathbf{Y}_{J,J+1,M} + F(r)_{J-}^L\mathbf{Y}_{J,J-1,M}, \quad \text{with } L \text{ integer } (l = J \pm 1) \tag{136}$$

We can furthermore specify the transverse vector-field, like the longitudinal field above, by using the expression of the curl of the field **T** so that:

$$\mathbf{T}_{J,M} = \sqrt{\frac{J}{2J+1}}(\mathrm{d}/\mathrm{d}r - J/r)\Phi_J^T\mathbf{Y}_{J,J+1,M} + \sqrt{\frac{J+1}{2J+1}}(\mathrm{d}/\mathrm{d}r + (J+1)/r)\Phi_J^T\mathbf{Y}_{J,J-1,M} \tag{137}$$

where $\phi_J^T = F_{J,J}(r)$ and, concerning the longitudinal field, $F(r)_{J+}^L, F(r)_{J-}^L$ are given by:

$$F(r)_{J+}^L = -\sqrt{\frac{J}{2J+1}}(\mathrm{d}/dr - J/r)\Phi_J^L \tag{138}$$

and

$$F(r)_{J+}^L = -\sqrt{\frac{J}{2J+1}}(\mathrm{d}/\mathrm{d}r + (J+1)/r)\Phi_J^L \tag{139}$$

We can now bring the connection of these vector fields to our electron functions u, v:

$$u(r)_J = \sqrt{\frac{J}{2J+1}}\Phi_J^T - \sqrt{\frac{J+1}{2J+1}}\Phi_J^L \tag{140}$$

and

$$v(r)_J = \sqrt{\frac{J}{2J+1}}\Phi_J^L + \sqrt{\frac{J+1}{2J+1}}\Phi_J^T \tag{141}$$

with the transition current being obtained by equating the coefficient of $\mathbf{Y}_{J,l,M}$ above:

$$\mathbf{j}_\alpha = \sum_{J,l=J\pm1,M} F_{\alpha,J,l}\mathbf{Y}_{J,l,M} \tag{142}$$

We shall finish the appendix by just giving the first terms for $F_{J,M}$:

$$F_{1,0} = -(4\pi3)^{-1/2}re_{-r}2e^{-2r} = \exp[-3r](-3 - r)/\sqrt{4\pi} \tag{143}$$

and

$$\begin{aligned}F_{1,2} &= -(4\pi 3/2)^{-1/2} re_{-r}2e^{-2r}\\ &\quad -(4\pi)^{-1/2}e^{-2r}re^{-r}(2/3)^{1/2}\\ &= \exp[-3r]r\sqrt{2/3}/\sqrt{4\pi}\end{aligned} \tag{144}$$

and therefore

$$(\mathrm{d}/\mathrm{d}r - 1/r)u_1 = F_{1,2} = \exp[-3r]r\sqrt{2/3}/\sqrt{4\pi} \tag{145}$$

and similar for v_1.

Appendix 5: Gaussian expansions and numerical calculations

In the following, we want to be able to compare results with standard DFT calculations using Gaussian functions. Hence, we shall, for the purpose of comparisons, introduce Gaussian expansions of the wavefunctions and similarly of the density ρ and its derivative that are also taken as Gaussian like. It is thus natural to start from the current expression:

$$j^L_{ki} = \nabla_r \int \mathrm{d}r'^3 \rho(r')^A_{ki} iE_{ki}/((r_) 4\pi\hbar)Y_{J,J-1,M} \tag{146}$$

and each Gaussian term now gets a radial form:

$$w(r) = r^{-A}\int_0^r \mathrm{d}r' r'^A \rho(r')C' \tag{147}$$

The argument from Ref. [13] that concerns the finiteness of the integrals above, independent of the sign of A, is still valid. Actually, extending the upper integration limit to infinity renders these Gaussian integrals manageable, such that:

$$\int_0^{\mathrm{inf}} \mathrm{e}^{-\lambda x^2}x^k = 1/2\lambda^{-(k+1)/m}/\Gamma((k+1/m) \tag{148}$$

showing that no singularities are occurring in this formalism. The integrals, which we shall use, are of the form:

$$Q(r) = -\sum_i \int \mathrm{d}r' \int \mathrm{d}r'' \psi_i(r)^* G_i(r,r')V_e(r',r'')\psi_i(r'') \tag{149}$$

which can be simplified, using the procedures of Eqs. 103 and 106, to:

$$r^{-A}\int_0^r \mathrm{d}r'(r'^A)C\int_0^{r'} \mathrm{d}r'' \mathrm{e}^{[-r''^2]} \tag{150}$$

where $A = J + 1$ corresponds to the vector spherical harmonics to be $Y_{J,J-1,M}$ but, in the case of $A = -J$, becomes $Y_{J,J+1,M}$. Considering just one term (diagonal) in a Gaussian expansion of an electron density (an ordinary, non-transition density) $\rho(r)_{kk}$, we can use the above formula to get:

$$\frac{j(r)^L_{kk}}{E_{kk}} = \int \mathrm{d}r'^3 \nabla'_r \rho(r')_{kk} i/84\pi\hbar \tag{151}$$

where

$$\begin{aligned}\nabla_r[\rho(r)] &= \nabla_r(F(r)Y_{JM})\\ &= -\sqrt{(J+1)/(2J+1)}(\mathrm{d}/\mathrm{d}r - J/r)F(r)Y_{J,J+1,M}\\ &\quad + \sqrt{J/(2J+1)}(\mathrm{d}/\mathrm{d}r - J/r)F(r)Y_{J,J-1,M}\end{aligned} \tag{152}$$

The two terms correspond to $A = -J$ and $A = J + 1$, respectively. Terms with negative A can be eliminated in the radial integral, where the F-functions now are of the Gaussian type. This can be seen by using a recursive procedure, repeated some times:

$$i^n erfc(z) = -z/ni^{n-1}erfc(z) + 1/(2n)i^{n-2}erfc(z) \tag{153}$$

or

$$\begin{aligned}2(n+1)(n+2)i^{n+2}erfc(z) &= (2n+1+2z^2)erfc(z)\\ &\quad - 1/2i^{n-3}erfc(z)\end{aligned} \tag{154}$$

where *erfc* is the error function.

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