Methods for electronic-structure calculations - an overview from a reduced-density-matrix point of view

P. Ziesche$^1$ and F. Tasnádi$^2$

$^1$Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany

$^2$Leibniz-Institut für Festkörper- und Werkstoffforschung, Helmholtzstr. 20, D-01069 Dresden, Germany, and University of Debrecen, Hungary

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The methods of quantum chemistry and solid state theory to solve the many-body problem are reviewed. We start with the definitions of reduced density matrices, their properties (contraction sum rules, spectral resolutions, cumulant expansion, $N$-representability), and their determining equations (contracted Schrödinger equations) and we summarize recent extensions and generalizations of the traditional quantum chemical methods, of the density functional theory, and of the quasi-particle theory: from finite to extended systems (incremental method), from density to density matrix (density matrix functional theory), from weak to strong correlation (dynamical mean field theory), from homogeneous (Kimball-Overhauser approach) to inhomogeneous and finite systems. Measures of the correlation strength are discussed. The cumulant two-body reduced density matrix proves to be a key quantity. Its spectral resolution contains geminals, being possibly the solutions of an approximate effective two-body equation, and the idea is sketched of how its contraction sum rule can be used for a variational treatment.

Keywords: many-body theory, reduced density matrices, spectral resolution, geminals, cumulant expansion, thermodynamic limit

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In the electron theory of atoms, molecules, clusters, and solids ($N$ electrons are confined to a volume $\Omega$) the pairwise Coulomb repulsion between electrons together with the Pauli ‘repulsion’ between electrons with parallel spins causes the complex phenomenon of electron correlation\cite{1}-\cite{22}. The problem is, to calculate this electron correlation from first principles. Even within the simplifying non-relativistic description and within the Born-Oppenheimer approximation, this problem can not be solved exactly. In some cases, correlation beyond the Hartree-Fock approximation causes only quantitative changes, but there are other cases, where it makes qualitative changes. So, electron correlation let exist the dimers $F_2$ and $Hg_2$, or it gives the correct sign for the dipole moment of CO. Electron correlation allows a solid to be a metal (in the Hartree-Fock approximation the density of states vanishes at the Fermi energy according to $\sim 1/\ln |\varepsilon - \varepsilon_F|$). Correlation brings the Curie temperature of ferromagnets down to the experimental values (in the Hartree-Fock approximation they are much too high). Electron correlation is important for the ground states of transition-metal oxides to be insulating or metallic, ferro- or antiferro-magnetic. Correlation has its peculiarities or needs different computational methods for closed-shell systems and open-shell systems, for finite and extended systems, for systems near and far from the equilibrium (defined by vanishing Hellmann-Feynman forces), for the ground state (GS) and for excited states (for a solid, this means its quasi-particle band structure), for different types of solids, for weak or moderate correlation (as for sp metals and semiconductors) and strong correlation (as for systems with open d-shells or open f-shells, e.g., transition metal oxides and rare earth or actinide systems, cf. Appendix). Here we focus on the GS. Its correlation shows up in the many-body (MB) wavefunction (WF) of the GS (e.g. in a Jastrow factor in front of a Slater determinant) or in the correlation energy (being unfortunately not sensitive to distinguish between weak and strong electron correlation) or in quantum-kinematical quantities, which follow from the MB WF by integration over most of the variables leaving only a few of them.
unintegrated. Thus hierarchies of reduced densities (RDs) $\rho_1, \rho_2, \ldots$ and reduced density matrices (RDMs) $\gamma_1, \gamma_2, \ldots$ arise with the advantage to allow a distinction between weak and strong correlation. Therefore they are used to define measures of the correlation strength. One possibility is the correlation induced non-idempotency of the 1-body RDM (1-matrix) $\gamma_1$. Another possibility is to derive correlation influenced particle-number fluctuations from the pair density (PD) $\rho_2$ in parts of the system; the conclusion is: correlation suppresses such fluctuations [1], p. 157, [23].

Important issues of the RDM theory are listed in the following: the contraction properties of the RDMs $\gamma_1, \gamma_2, \ldots$ and their cumulant expansions (Sec.2), parts of the total energy as functionals of RDs or RDMs (Sec.3), the hierarchy of contracted Schrödinger equations (CSEs) [what means the equation for $\gamma_1$ contains $\gamma_2$ and $\gamma_3$, the equation for $\gamma_2$ contains $\gamma_3$ and $\gamma_4$, $\cdots$] (Sec.4), and the size-extensivity [because only size-extensive quantities are compatible with the thermodynamic limit (TDL), which means $N, \Omega \to \infty, N/\Omega = \text{const}$] (Sec.5). Finally a comprehensive summary of recent developments in the calculational treatment of the many-electron problem is given (Sec.6). Thereby, “old” methods to calculate the electronic structure like the WF based methods [namely, configuration interaction (CI), coupled cluster (CC), Møller-Plesset (MP), and quantum Monte Carlo (QMC) for finite systems] and the density based density functional theory (DFT) [24, 25] and the Green’s function based quasi-particle theory (QPT) [26] for both finite and extended systems are compared with some “new” methods like the WF based incremental method [27, 28, 29] (thereby the nearsightedness of electron correlation [30] is used) or the 1-matrix based density-matrix functional theory (DMFT) (being conceptionally simpler and yielding more informations than the DFT) [31, 32, 33, 34], and also extensions towards strong correlation (Sec.VI(c),(i), Appendix). Within the RDM theory [5, 6, 7, 8], there seem to be three possibly prospective (?) developments: (i) the $N$-representability studies (Kummer variety, Coleman’s algorithm, linear inequalities) [8], (ii) the CSE method for finite systems [7], p. 85, 117, 139, [35, 36, 37] including critical discussions of the thereby used ‘reconstructions’ [38, 39, 40] and alternative suggestions (Kutzelnigg [40]), and (iii) the Kimball-Overhauser approach for the PD of the homogeneous electron gas (HEG) in terms of 2-body WFs (geminals), cf. [41, 42, 43].
and refs. therein. - The paper contains also open questions with the intention to stimulate further research.

| TABLE I: List of acronyms |
|---------------------------|
| AGP | antisymmetrized geminal power | MB | many-body |
| CC | coupled cluster | MP | Møller-Plesset |
| CI | configurational interaction | MR | multi reference |
| CSE | contracted Schrödinger equation | PDFT | pair density functional theory |
| DFT | density functional theory | QMC | quantum Monte Carlo |
| DMFT | density matrix functional theory | QPT | quasi-particle theory |
| ELF | electron localization function | RD | reduced density |
| GGA | generalized gradient approximation | RDM | reduced density matrix |
| GS | ground state | SR | sum rule |
| HEG | homogeneous electron gas | TDL | thermodynamic limit |
| KS | Kohn-Sham | XC | exchange-correlation |
| LDA | local density approximation | WF | wave function |

II. BASIC QUANTUM KINEMATICS

The GS of a non-relativistic $N$-electron system in Born-Oppenheimer approximation is described by a $N$-body WF $\Psi(1, \ldots, N)$ with $1 = (r_1, \sigma_1)$ and $\int d1 = \int d^3r_1 \sum_{\sigma_1}$ or equivalently by a hierarchy of hermitian RDMs $\gamma_1, \gamma_2, \gamma_3, \ldots$ [first introduced by K. Husimi [44]] with the following contraction sum rules (SRs)

$$\gamma_1(1|1') = \int \frac{d^2}{N-1} \gamma_2(1|1', 2|2), \quad \gamma_2(1|1', 2|2') = \int \frac{d^3}{N-2} \gamma_3(1|1', 2|2', 3|3), \ldots$$

or $C \gamma_2 = (N-1) \gamma_1, C \gamma_3 = (N-2) \gamma_2, \ldots$ for short, i.e. the contraction operator $C$ makes the last variable pair diagonal ($i' = i$) and integrates it ($\int di$). This chain $\gamma_N = \Psi \Psi^* \rightarrow \cdots \rightarrow \gamma_3 \rightarrow \gamma_2 \rightarrow \gamma_1$ is called $N$-representability, $\Psi^* = \Psi^*(1', \ldots, N')$. It becomes infinitely long in the TDL. Note $\text{Tr} \gamma_1 = N, \text{Tr} \gamma_2 = N(N-1), \cdots, \text{Tr} \gamma_N = N!$. The diagonal elements of
\( \gamma_1, \gamma_2, \gamma_3, \cdots \) are the density \( \rho_1 \), the pair density (PD) \( \rho_2 \) [containing the Fermi hole for the spin-parallel electron pairs and the Coulomb hole for the spin-antiparallel electron pairs], the triple density \( \rho_3, \cdots \):

\[
\rho_1(1) = \gamma_1(1|1), \quad \rho_2(1, 2) = \gamma_2(1|1, 2|2), \quad \rho_3(1, 2, 3) = \gamma_3(1|1, 2|2, 3|3), \cdots
\]  

(2)

or \( \rho_1 = D\gamma_1, \rho_2 = D\gamma_2, \rho_3 = D\gamma_3, \cdots \), i.e. the diagonal operator D makes all the variable pairs diagonal \((1'=1, 2'=2, \cdots)\). Note \( \rho_i \geq 0 \). If \( X \) is a certain part of the system (e.g. a Daudel loge, refs. on this loge theory are in Ref. [45, 46]), then

\[
N_X = \int_X d1 \rho_1(1), \quad \left( \frac{N}{2} \right)_X = \int_X \frac{d1d2}{2!} \rho_2(1, 2), \cdots
\]  

(3)

have respectively the meaning of the average number of particles in \( X \), the average number of particle pairs in \( X \) etc., approaching \( N, \left( \frac{N}{2} \right) \), \( \cdots \) for \( X \to \infty \). The term ‘average number of particles in \( X \)’ means: the number of particles in \( X \) fluctuates. In lowest order, such fluctuations are described by the mean squared deviation \( \Delta N_X \). They are determined by the 2-body function \( w_2(1, 2) \) [defined by \( \rho_2(1, 2) = \rho_1(1)\rho_1(2) - w_2(1, 2) \)] according to

\[
\frac{(\Delta N_X)^2}{N_X} = 1 - \frac{1}{N_X} \int_X d1 \int_X d2 \ w_2(1, 2), \quad \int_X d1 \int_X d2 \ w_2(1, 2) = N.
\]  

(4)

\( w_2(1, 2) \) is size-extensively normalized. Particle-number fluctuations can be described in more detail by \( P_X(M) \), the probability of finding \( M(= 0, 1, \cdots, N) \) particles in \( X \) with

\[
\sum_{M=0}^{N} P_X(M) = 1, \quad \sum_{M=0}^{N} P_X(M)M = N_X, \quad \sum_{M=0}^{N} P_X(M)(M-N_X)^2 = (\Delta N_X)^2.
\]  

(5)

The example [23]

\[
P_X(1) = \int_X d1 \rho_1(1) - \frac{1}{1!} \int_X d1 \int_X d2 \rho_2(1, 2) + \frac{1}{2!} \int_X d1 \int_X d2 \int_X d3 \rho_3(1, 2, 3) - \cdots
\]  

(6)

shows, how e.g. \( P_X(1) \) follows from the reduced densities. For other values of \( M \) cf. [23]. An approximate expression needs only \( \rho_1 \) and \( \rho_2 \), namely \( P_X(M) \sim e^{-\beta(M-\alpha)^2} \) with distribution parameters \( \alpha \) and \( \beta \) determined by \( N_X \) and \( \Delta N_X \). [This expression maximizes the entropy \(-\sum_{M} P_X(M) \ln P_X(M)\) under the constraints of given \( N_X \) and \( \Delta N_X \).] The fluctuation analysis of finite and extended systems based on this approximation shows that
'(strong) correlation (strongly) suppresses fluctuations' \cite{[1, 23]}; for attractive interaction (of
the Calogero-Sutherland model = one-dimensional Fermi gas with $1/x^2_{ij}$ interaction), they
are enhanced \cite{[47]}. For the peculiarities of strong electron correlations cf. Appendix. - The
‘on-top’ curvature of the Fermi hole is used as a local measure of the correlation strength \cite{[46]}.
It is also derived an ‘electron localization function (ELF)’ \cite{[48]}; an alternative is introduced
in Ref.\cite{[49]}.

Because the RDMs are hermitian, they can be diagonalized with

$$
\gamma_1(1|1') = \sum_\kappa \psi_\kappa(1) \nu_\kappa \psi_\kappa^*(1'), \quad 0 < \nu_\kappa < 1, \quad \sum_\kappa \nu_\kappa = N
$$

as the simplest example. The $\psi_\kappa(1)$ are called natural orbitals (more precisely spin-orbitals)
with natural occupancies $\nu_\kappa$. For the HEG, the $\psi_\kappa(1)$ are plane waves and the $\nu_\kappa$
yield the momentum distribution $n(k)$, recently parametrized in Ref.\cite{[50]}. The occupancies are only
exceptionally idempotent, in general they are non-idempotent: $\nu^2_\kappa < \nu_\kappa$ and $\sum_\kappa \nu^2_\kappa < N$.
Because P.-O. Löwdin has asked for the meaning of $\sum_\kappa \nu^2_\kappa = \text{Tr} \gamma^2_1 \cite{[51]}$, the quantity

$$
c_2 = 1 - \text{tr} \gamma^2_1 = 1 - \frac{1}{N} \sum_\kappa \nu^2_\kappa, \quad 0 < c_2 < 1
$$

will be referred to as Löwdin parameter (with $\text{tr} = \frac{1}{N} \text{Tr}$). For non-interacting single-reference
cases (only one Slater determinant) and therefore idempotent occupancies $\nu_\kappa = 0$ or 1,
this parameter vanishes. Interaction then causes a correlation tail in the CI expansion
with a lot of additional Slater determinants beyond the leading Slater determinant. This
makes the $\nu_\kappa$ non-idempotent, thus $c_2 > 0$. So, $c_2$ is another measure of the correlation
strength \cite{[52, 53]}. An increasing weight of the CI correlation tail increases also $c_2$ (with
perhaps weak, moderate, and strong correlation for $c_2 \ll 1/2$, $c_2 \approx 1/2$, and $c_2 \gg 1/2$,
respectively). Thereby the CI expansion is thought to be unique (basis set independent) by
representing it through natural spin orbitals. Often one has to start with a multi-reference
(MR) state, a sum of several Slater determinants to correctly describe, e.g., a dissociation
limit or nearly degeneracy. Then the Löwdin parameter is already non-zero for ‘no CI
correlation tail’ ($c_{\text{MR}} > 0$. For this description the term ‘non-dynamical or static correlation’
is used) following Clementi and Corongiu \cite{[102]}. Full CI with its additional correlation tail
('dynamical correlation') makes then \( c_2 > c_{\text{MR}} \). For a solid, \( \nu_\kappa \) contains the occupancy band structure \([54]\). The 2-body analog of Eq.(7) is the spectral resolution of the 2-matrix \( \gamma_2 \), containing antisymmetric 2-body WFs (natural geminals). Are they the solutions of a 2-body Schrödinger equation with an appropriately screened Coulomb repulsion (similar as this is the case with the Kimball-Overhauser approach for the HEG \([41]\))?  

An important aspect of the quantum kinematics is the cumulant expansion of RDMs and RDs \([55]\). Its most compact representation uses generating functionals, cf. e.g. P. Ziesche in \([7]\), p. 33. For the simplest case of the 2-matrix this means

\[
\gamma_2(1|1',2|2') = \gamma_1(1|1')\gamma_1(2|2') - \gamma_1(1|2')\gamma_1(2|1') - \chi_2(1|1',2|2')
\]  

(9)

or \( \gamma_2 = A\gamma_1\gamma_1 - \chi_2 \) for short (\( A = \) antisymmetrizer). The factorized (or disconnected) terms are the generalized (because the natural occupancies are non-idempotent) Hartree-Fock part of \( \gamma_2 \) with \( \text{Tr}_{\gamma_2}^{\text{HF}} = N(N-1) + Nc_2 \). The non-factorizable remainder \( \chi_2 \) is called cumulant 2-matrix. In perturbation theory, \( \chi_2 \) is given by (size-extensive) linked diagrams; therefore it is also called connected part of \( \gamma_2 \). [An equation similar to Eq.(9) defines the cumulant part of the 2-body Green’s function.] The above mentioned contraction SR \( C\gamma_2 = (N-1)\gamma_1 \) (which is not size-extensive) is transformed to \( C\chi_2 = \gamma_1 - C\gamma_1^2 \) or

\[
\int d^2 \chi_2(1|1',2|2) = \gamma_1(1|1') - \int d^2 \gamma_1(1|2')\gamma_1(2|1') = \sum_\kappa \psi_\kappa(1)\nu_\kappa(1 - \nu_\kappa)\psi_\kappa^*(1').
\]  

(10)

The invariance of the rhs under the exchange \( \nu_\kappa \leftrightarrow (1 - \nu_\kappa) \) is called particle-hole symmetry \([56]\). Eq.(10) contains the normalization SR

\[
\text{tr} \chi_2 = \frac{1}{N} \sum_\kappa \nu_\kappa(1 - \nu_\kappa) = c_2; \quad s = -\frac{1}{N} \sum_\kappa [\nu_\kappa \ln \nu_\kappa + (1 - \nu_\kappa) \ln(1 - \nu_\kappa)].
\]  

(11)

Thus the Löwdin parameter \( c_2 \) measures the non-idempotency of the natural occupancies \( \nu_\kappa \) and simultaneously the normalization of the cumulant 2-matrix \( \chi_2 \) per particle, thereby not affecting the normalization of the total 2-matrix \( \gamma_2 \). \( s \) defines the particle-hole symmetric correlation entropy \([50, 52]\). For the PD \( \rho_2 \) the cumulant expansion Eq.(9) means

\[
\rho_2(1,2) = \rho_1(1)\rho_1(2) - \gamma_1(1|2)\gamma_1(2|1) - u_2(1,2), \quad u_2(1,2) = \chi_2(1|1,2|2).
\]  

(12)
$u_2$ may be addressed as cumulant PD. Comparison with Eq.(11) shows $w_2(1,2) = \gamma_1(1|2)\gamma_1(2|1) + u_2(1,2)$, being thus the exchange including cumulant PD.

If $\chi_2$ is available from perturbation theory or from some effective 2-body theory, then the SR Eq.(10) allows one to determine the 1-matrix $\gamma_1$ by means of diagonalizing Eq.(10). The resulting quadratic equation $\lambda_\kappa = \nu_\kappa(1 - \nu_\kappa)$ is solved by $\nu_\kappa^{\pm} = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \lambda_\kappa}$. Associating certain $\kappa$’s to $+$ and all the others to $-$, yields occupancies $\nu_\kappa > \frac{1}{2}$ and $\nu_\kappa < \frac{1}{2}$ respectively, such that $\sum_\kappa \nu_\kappa = N$. [For the low-density HEG($r_s \gg 1$), i.e. for the Wigner crystal only $\nu_\kappa^{-}$ has a physical meaning and it is $\lambda_\kappa \ll 1$, thus $\nu_\kappa^{-} \approx \lambda_\kappa$.] Let us denote the described procedure by $\gamma_1 = \tilde{C}\chi_2$. With this $\gamma_1$ the exact MB kinetic energy $T$ and the Löwdin parameter $c_2$ can be calculated and also the PD $\rho_2$, which is needed for the interaction energy $V_{\text{int}}$ and for the fluctuation analysis (both in direct and momentum space). So, the cumulant 2-matrix $\chi_2$ is the most interesting quantum kinematic quantity. Although it is a key quantity, unfortunately not much is known about it. Questions:

• What is known about the spectral resolution of the cumulant 2-matrix $\chi_2$?

$$\chi_2(1|1',2|2') = \frac{1}{2!} \sum_K \psi_K(1,2)\mu_K\psi_K^*(1',2'), \quad \frac{1}{N} \sum_K \mu_K = c_2. \tag{13}$$

Which values are possible for the cumulant occupancies $\mu_K$?

• $\gamma_2$ is $N$-representable. What are the consequences for $\chi_2$?

• What are the peculiarities of $\chi_2$ for metals (for the high-density HEG cf. 57), quasi-one-dimensional charge-density-wave conductors, semiconductors, (band, Peierls, charge-transfer, Mott-Hubbard) insulators, superconductors (off-diagonal-long-range order), ferro/antiferro-magnets, ferroelectric? For cases of strong electron correlation cf. Appendix.

• What are the peculiarities of $\chi_2$ for cases, where one of the occupancies of $\gamma_2$ is very large. There exists a rich literature on antisymmetrized geminal power (AGP) WFs, cf. 6, 58. M. Rosina has studied the 2-matrix $\gamma_2$ of the AGP WF 11. The AGP function is a flexible ansatz for fermion systems with arbitrary $N$. Extreme AGP
WFs have (for large $N$) very large 2-matrix occupancies equaling $[N/2]$ \cite{6}, p. 35, \cite{59}. The GS of Be has a large 2-matrix occupancy ($>1$) (V.H. Smith, priv. commun.). What does all this mean for the cumulant occupancies $\mu_K$?

- Electron correlation is discussed in terms of its nearsightedness \cite{30}. How does this show up by $\chi_2$?

A drawback of $\chi_2$ is that the positivity condition $\rho_2 \geq 0$ becomes more complicated.

The normalization and contraction of $\chi_3$ yield $\text{Tr} \chi_3 = 2 \sum_\nu \nu_\nu (1 - \nu_\nu) (1 - 2 \nu_\nu) \equiv Nc_3$ and $C \chi_3 (1|1', 2|2'; 3|3') = 2 \chi_2 (1|1', 2|2') - [A' C \chi_2 (1|1', 2|3) \chi_1 (3'|2') + \text{h.c.}],$ where the contraction operator $C$ makes $3' = 3$ and $\int d3$ as defined above, $A'$ is the antisymmetrizer with respect to the primed variables and h.c. means hermitian conjugate. Thereby integrals $\int d3 \psi_K (1, 3) \psi^*_K (3)$ appear, which describe the overlap of a natural orbital with a cumulant geminal.

### III. BASIC FUNCTIONALS

Explicitly defined functionals for the components of the GS energy $E$ are

$$T[\gamma_1] = \int d1 \ t(r_1) \gamma_1 (1|1') |_{\nu=1}, \quad t(r_1) = -\frac{1}{2} \frac{\partial^2}{\partial r_1^2},$$

$$V_{\text{ext}} [\rho_1] = \int d1 \ \rho_1 (1) v_{\text{ext}} (r_1), \quad V_{\text{int}} [\rho_2] = \int \frac{d1d2}{2!} \ \rho_2 (1, 2) v_{\text{int}} (r_{12}). \quad (14)$$

These are linear functionals. The generalized Hartree and Fock components of the interaction energy $V_{\text{int}}$ are the bilinear functionals

$$V_{\text{H}} [\rho_1] = \int \frac{d1d2}{2!} \ \rho_1 (1) \rho_2 (2) v_{\text{int}} (r_{12}), \quad V_{\text{F}} [\gamma_1] = \int \frac{d1d2}{2!} \ \gamma_1 (1|2) \gamma_1 (2|1) v_{\text{int}} (r_{12}). \quad (15)$$

Furthermore, the cumulant partitioning needs the linear functionals

$$V_{\text{FC}} [w_2] = -\int \frac{d1d2}{2!} \ w_2 (1, 2) v_{\text{int}} (r_{12}), \quad V_{\text{C}} [u_2] = -\int \frac{d1d2}{2!} \ u_2 (1, 2) v_{\text{int}} (r_{12}). \quad (16)$$

Then the interaction energy is given by

$$V_{\text{int}} [\rho_2] = V_{\text{H}} [\rho_1] + V_{\text{FC}} [w_2], \quad \rho_1 = \frac{\int d2 \rho_2}{N-1}, \quad w_2 = \rho_1^2 - \rho_2 \quad (17)$$
or
\[ V_{\text{int}}[\gamma_1, u_2] = V_H[\rho_1] + V_F[\gamma_1] + V_C[u_2], \quad \rho_1 = D\gamma_1 = \frac{\int d^2 u_2}{c_2}. \]  
(18)

Consequently, the total GS energy is
\[ E[\gamma_2] = T[\gamma_1] + V_{\text{ext}}[\rho_1] + V_H[\rho_1] + V_{FC}[u_2] \]
or
\[ \tilde{E}[\chi_2] = T[\gamma_1] + V_{\text{ext}}[\rho_1] + V_H[\rho_1] + V_F[\gamma_1] + V_C[u_2]. \]
(19)
(20)

The \(N^2\) terms of \(V_{\text{ext}}\) and \(V_H\) cancel each other. In the sum \(V_H + V_F\), the self-interaction terms cancel each other. In the sum \(V_F + V_C\) there is also a certain cancellation as it may be seen from the normalization \(\text{Tr}(\gamma_2^2 + u_2) = N\), which does not contain the Löwdin parameter \(c_2\). To find the GS, one has to minimize these functionals \(E[\gamma_2]\) or \(\tilde{E}[\chi_2]\), provided that the \(N\)-representability \([8]\) is taken into account: \(\gamma_2\) follows from \(\gamma_3\), \(\gamma_3\) from \(\gamma_4\) etc. by successive contractions, cf. Eq.\((1)\).

Other functionals implicitly defined by means of Levy’s constrained search \([60]\) are (i) for the well tried and widely used DFT
\[(T + V_{\text{int}})[\rho_1] = \min_{\Psi \to \rho_1} \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle, \quad \rho_1 = D\gamma_1, \quad \gamma_1 = \frac{C\gamma_2}{N - 1}, \ldots, \]
(21)
from which follows \((T + V_{FC})[\rho_1] = (T + V_{\text{int}})[\rho_1] - V_H[\rho_1],\) (ii) for the DMFT (under discussion)
\[ \hat{V}_{\text{int}}[\gamma_1] = \min_{\Psi \to \gamma_1} \langle \Psi | \hat{V}_{\text{int}} | \Psi \rangle, \quad \gamma_1 = \frac{C\gamma_2}{N - 1}, \ldots, \]
(22)
from which follows \(\hat{V}_C[\gamma_1] = \hat{V}_{\text{int}}[\gamma_1] - V_H[\rho_1] - V_F[\gamma_1],\) and (iii) for a possible pair-density functional theory (PDFT)
\[ \hat{T}[\rho_2] = \min_{\Psi \to \rho_2} \langle \Psi | \hat{T} | \Psi \rangle, \quad \rho_2 = D\gamma_2, \quad \gamma_2 = \frac{C\gamma_3}{N - 2}, \ldots. \]
(23)
The 1-matrix functional \(\hat{V}_{\text{int}}[\gamma_1]\) has the simple scaling property \(\hat{V}_{\text{int}}[\lambda\gamma_1] = \lambda \hat{V}_{\text{int}}[\gamma_1]\), where \(\gamma_1^\lambda(\mathbf{r}_1|\mathbf{r}_1') = \lambda^3 \gamma_1(\lambda \mathbf{r}_1|\lambda \mathbf{r}_1').\) The PD functional \(\hat{T}[\rho_2]\) has the simple scaling property \(\hat{T}[\lambda \rho_2] = \lambda^2 \hat{T}[\rho_2]\), where \(\rho_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \lambda^6 \rho_2(\lambda \mathbf{r}_1, \lambda \mathbf{r}_2).\) The reason of these simple scaling properties are the homogeneities of the corresponding operators \(\hat{V}_{\text{int}}\) and \(\hat{T}\) with degrees \(-1\) and \(-2,\)
respectively. These different degrees cause the more complicated scaling of the density functional \((T + V_{\text{int}})[\rho_1]\), where the constrained search involves both \(T\) and \(V_{\text{int}}\). To find approximate functionals for \(V_{\text{int}}[\gamma_1]\) and for \(T[\rho_2]\), one may search for approximate functionals \(\chi_2[\gamma_1]\) (as e.g. proposed by K. Yasuda) and \(\gamma_1[\rho_2]\), respectively. From the above introduced functionals follow the density functional

\[
E_{\text{DFT}}[\rho_1] = (T + V_{\text{int}})[\rho_1] + V_{\text{ext}}[\rho_1],
\]

the density-matrix (1-matrix) functional

\[
E_{\text{DMFT}}[\gamma_1] = T[\gamma_1] + V_{\text{ext}}[\rho_1] + \tilde{V}_{\text{int}}[\gamma_1],
\]

and the PD functional

\[
E_{\text{PDFT}}[\rho_2] = \tilde{T}[\rho_2] + V_{\text{ext}}[\rho_1] + V_{\text{int}}[\rho_2],
\]

to be minimized, cf. Sec.VI(c),(d),(e).

IV. BASIC EQUATIONS

In order to find the GS \(\Psi(1, \cdots, N)\), the starting point is the MB Schrödinger equation

\[
\hat{H}\Psi = E\Psi.
\]

From it follows the hierarchy of CSEs by multiplying it with \(\Psi^*\) and performing successively the \(N - 1\) contraction, the \(N - 2\) contraction etc.:

\[
\int d^2 \cdots \left(\hat{H} - E\right) \Psi \Psi^* |_{2'' = 2, 3'' = 3, \cdots} = 0,
\]

\[
\int d^3 \cdots \left(\hat{H} - E\right) \Psi \Psi^* |_{3'' = 3, 4'' = 4, \cdots} = 0, \cdots.
\]

On the lhs the RDMs \(\gamma_1, \gamma_2, \gamma_3, \cdots\) appear. Thereby the CSE for \(\gamma_1\) contains \(\gamma_2\) and \(\gamma_3\) (1st formula), therefore it is called 1,3-CSE; the CSE for \(\gamma_2\) contains \(\gamma_3\) and \(\gamma_4\) (2nd formula), called 2,4-CSE, \(\cdots\). Expressing these RDMs by their cumulants \(\chi_2, \chi_3, \cdots\) an equivalent hierarchy appears (no longer containing \(E\)); for a uniform notation one should define the 1-body ‘cumulant’ as \(\chi_1 \equiv \gamma_1\).

An equivalent writing of the Schrödinger equation is

\[
E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad \langle \Psi | \Psi \rangle = N!.
\]

An equivalent writing of the hierarchy is

\[
E = \min_{\gamma_2} E[\gamma_2], \quad \gamma_2 = \frac{C\gamma_3}{N + 1}, \cdots, \quad \text{Tr} \gamma_i = N(N - 1) \cdots (N + 1 - i).
\]

The size-extensive version of Eq.\[25\] is

\[
e = \min_{\gamma_2} \tilde{\gamma}_2, \quad \gamma_2 = C\chi_3, \cdots, \quad \text{tr} \gamma_i = c_i \text{ with } \tilde{\gamma}_2 = \tilde{E}[\chi_2]/N, \quad \text{cf. Eq.\[20\]. It survives the TDL (\(N, \Omega \to \infty, N/\Omega = \text{const}\).}

Using the relation \(\gamma_1 = C\chi_2\) described after Eq.\[12\], the total energy becomes a functional of \(\chi_2\), which in its spectral resolution provides geminals \(\psi_K\) and occupancies \(\mu_K\) as variational parameters. Does this procedure give a link to the Kimball-Overhauser approach?
V. SIZE-EXTENSITIVITY AND THERMODYNAMIC LIMIT

Solid state theory considers extended systems, which result from finite systems (N electrons confined in a volume Ω) through the TDL. In the terms of thermodynamics one has to distinguish intensive quantities, e.g. the density ρ₁, and extensive quantities, which are proportional to N, like the normalization of ρ₁ or the kinetic energy T. Amongst the quantities listed above are also such ones, which contain terms proportional to N². Examples are V_{ext} and V_H. Fortunately their sum is size-extensive, what makes the total energy E also size-extensive. Thus the ratio e = E/N survives the TDL, it defines the bulk energy. Another example is the normalization of the PD ρ₂, where also N² terms are present. This deficiency is ‘removed’ by considering the cumulants of ρ₂. Both w₂(1, 2) and u₂(1, 2) are size-extensively normalized and the cumulant 2-matrix χ₂ is size-extensively contractable.

What happens with the equation \( \hat{H} \Psi = E \Psi \) in the TDL? One may divide it by N and use the bulk energy e = E/N on the rhs, but \( \hat{H}/N \) has no meaning in the TDL. Fortunately the hierarchy [being finite for finite N, Ω] only becomes infinitely long in the TDL. This hierarchy has to be solved at least approximately. Even if this has been done yielding the GS properties χ₂ (and from it also γ₁, ρ₁, ρ₂) and e, the question arises, how to obtain such important solid state properties as the quasi-particle band structure with its band gap and particle-hole bound states (in the case of a semiconductor) and its Fermi surface and plasmons (in the case of metals) and its effective masses and life-times. This task goes beyond RDM theory. It needs the Green’s function based QPT, cf. Sec.VI(i).

The TDL let emerge solid state properties having no counterparts in small clusters. Such properties are long-range ordering phenomena like ferromagnetism or other strong-electron-correlation phenomena like metal-insulator transitions, Wigner-charge ordering, coexistence of ferromagnetism and superconductivity, heavy fermions, quantum criticality, cf. Appendix.

VI. CLASSIFICATION OF CALCULATIONAL METHODS

Amongst the calculational methods one may distinguish methods for finite systems (atoms, molecules, clusters) and for extended systems (crystalline solids) including jellium.
models. Another classification is: methods based on the many-body WF and non-WF based methods, cf. Table II.

TABLE II: Methods to calculate the electronic structure. The symbols (!), (?), (??) mean ‘well tried’, ‘option’, ‘idea’, respectively.

|                | finite       | extended   |
|----------------|--------------|------------|
| WF based       | CI,CC,MP(!)  | → ?        |
|                | QMC(!)       | → ?        |
| non-WF based   | DFT(!)       | DFT(!)     |
|                | DMFT(?)      | DMFT(?)    |
|                | PDFT(??)     | PDFT(??)   |
|                | Coleman(?)   | → ?        |
|                | CSE(?)       | → ?        |
|                | ? ← Kimball-Overhauser |          |
|                | QPT(!)       | QPT(!)     |

(a) There are recent attempts to make the well-tried quantum-chemical methods, e.g. CC, applicable also to crystalline solids. This subject was thoroughly discussed at [20], especially by P. Fulde, B. Paulus, and U. Birkenheuer (incremental method). With this method (based on localized Hartree-Fock orbitals and a ‘constrained’ CI scheme), GS properties of insulating solids were calculated [27]. One extension of the incremental scheme concerns metals and strongly correlated systems. Thereby the problems appear of how to construct local orbitals in metals, how the incremental scheme works with these orbitals and how to handle the high degeneracy near the Fermi edges (with a MR method) [63]. This allows the method to be applied to the strongly correlated dissociation limit and describe a metal-insulator transition [64]. Another extension of the incremental scheme aims to compute correlated wave functions and energies of both valence and conduction bands [28, 29]. Thus the band gap for periodic
insulating systems including the effect of electron correlation can be determined. First results are available for diamond and polyacetylene [65].

R.J. Bartlett says “CC theory offers the natural vehicle for transferring 1st-principle electronic structure informations into material modeling”, in [3b], p. 219. Because electron correlation is ‘short-sighted’ (W. Kohn [30]) a localized correlation treatment is developed using natural bond orbitals [66].

(b) For the QMC method in general cf. [12]. In order to reliably predict materials properties, a QMC method using Hubbard-Stratonovich auxiliary fields has been developed [67]. This MB method is aimed at treating electron correlations in real materials. A first application concerns bulk Si. Slater determinants from DFT calculations were used as the trial WFs. The cohesive energy is comparable to (or better than) the best existing theoretical results.

In contrast to the WF based methods (a) and (b), the methods (c)-(i) are motivated by asking “Is the WF not a monster containing too much information, why one should struggle with it? Let us better concentrate on the lowest order RDMs, namely $\gamma_1, \gamma_2$ and their positivity properties and more general their $N$-representability (Coulson’s challenge)”, [8].

(c) DFT [24] uses the density $\rho_1$ [which has its charme and power [25]] as basic quantity. In its Kohn-Sham (KS) version, the non-idempotent 1-matrix $\gamma_1$ is the sum of an idempotent part $\gamma_1^{KS}$, corresponding to a non-interacting system with the kinetic energy $T_{KS}[\rho_1]$, and a remainder, such that (i) $D\gamma_1^{KS} = \sum_{\kappa}^{occ} |\psi_\kappa(1)|^2$ (these KS orbitals $\psi_\kappa$ are not natural orbitals!) gives the correct GS density $\rho_1$ of the interacting system (although $\gamma_1^{KS}$ is not the correct 1-matrix), (ii) the equation $(T + V_{\text{int}})[\rho_1] = T_{KS}[\rho_1] + E_{XC}[\rho_1]$ defines the exchange-correlation (XC) functional $E_{XC}[\rho_1]$ to be approximated (LDA, GGA, · · ·), and (iii) the minimization of $E_{\text{DFT}}[\rho_1]$ yields an effective 1-body Schrödinger equation with an XC potential $v_{XC}(1) = \delta E_{XC}[\rho_1]/\delta \rho_1(1)$. Finally, its solution gives (together with the aufbau principle) the density $\rho_1(1)$ and the total energy $E$. Besides Lagrange multipliers $\varepsilon_\kappa$ appear, which surprisingly approximate the
quasi-particle band structure of sp metals as (from a conceptional point of view) illegitimate children of the KS-DFT (W. Kohn). But for semiconductors their KS-DFT band gaps are too small and for heavy-fermion systems the experimental effective masses are much larger than the KS-DFT ones. DFT goes beyond the correlation neglecting Hartree-Fock approximation. It is well-tried and widely used for both finite and extended (metallic and semiconducting/insulating) systems, cf. e.g. [4].

The interconnections between DFT and CC theory are studied (R.J. Bartlett at [18]). Activities are going on trying to remove deficiencies and failures of this method (e.g. the van-der-Waals interaction [68], the problems listed under (d), the asymptotic behavior of the XC potential [69]), and to generalize it, e.g. DFT for MR cases (A. Savin at [18]), time-dependent DFT [70] and its relation to QPT [71], DFT for excited states [72], DFT for transport properties [73].

In particular the originally used LDA [based on the HEG and being the Thomas-Fermi approximation on a higher level] is modified (i) by climbing the ‘Jacob’s ladder’ via GGA and Meta-GGA up to Hyper-GGA, which are non-empirical approximations for $E_{XC}[\rho]$ designed for molecules and solids [74], (ii) by studying orbital functionals (optimized effective potential method, the DF method in 3rd generation), cf. e.g. [75], and (iii) by taking into account peculiarities of strong correlation (Appendix), which suppresses charge fluctuations, thus localizes electrons and therefore favors insulating behavior. Strong electron correlation is often treated with the help of the Hubbard model (containing the on-site Coulomb repulsion $U$), the $t$-$J$ model, the Anderson model (including attempts to determine model parameters from 1st principles [76]) or the orbital model [77] and the density-matrix renormalization group [78].

One way for (iii) is the combination with the Hubbard model (LDA+U); its possible link to 1-body Green’s function theory is discussed in Ref. [79], where a density functional application to strongly correlated electron systems is presented. Another way is the combination with the dynamical mean field theory of strongly correlated fermion systems [80]. This allows realistic calculations of transition metal oxides and f-electron materials, e.g. the Mott-Hubbard transition of $V_2O_3$, the volume collapse transition of Ce, the magnetic properties of LiV$_2$O$_4$, and
the photoemission spectra of SrVO$_3$ and CaVO$_3$[81].

(d) DMFT uses the 1-matrix $\gamma_1$ as basic quantity [31]. Unlike DFT, it does not need a (non-interacting) reference system, but it needs an approximation for $\tilde{V}_{\text{int}}[\gamma_1]$ or $\tilde{V}_C[\gamma_1]$, from which follows the functional $E_{\text{DMFT}}[\gamma_1]$. Its minimization yields $\gamma_1$ and $E$ (but not $\rho_2$ and in the case of solids not the band structure), cf. e.g. [82]. Each of the so far proposed approximations have their successes and shortcomings (e.g. violation of the positivity condition or of the contraction SR). Conditions for approximate 1-matrix functionals are in Ref. [32]. From a conceptional point of view, DMFT is simpler than DFT. The hope is that the new method is like DFT cheaper than CI, CC, MP and applies to both finite and extended (metallic and insulating) systems and that it can handle problems where DFT fails [83]:

- negative atomic ions are not bound, ionization potentials are too small,
- correlation energies of He($Z$) and Be($Z$) have not the correct large-$Z$ behavior, cf. [84],
- errors in the bond lengths and bond angles of some molecules, e.g. CH$_4$, H$_2$O, BH, O$_3$, Li$_2$, Be$_2$ (through this series, static correlation is progressively increasing),
- the reaction H$_2$ + H $\rightarrow$ H + H$_2$ is another MR case, it has no transition state in LDA and one that is too low with better functionals beyond LDA,
- wrong dissociation limits,
- cohesive energies of bulk metals are overestimated in LDA and underestimated in GGA,
- DFT poorly performs for polyacetylene fragments and oligoporphyrins, incorrectly predicting a triplet GS for polyacetylene [85].

There are links between DMFT and the RDM theory (reconstruction of the 2-matrix) [33] and between DMFT and the theory of antisymmetrized products of strongly orthogonal geminals [34]. For the geminal theory in general cf. [86].
(e) The possible PDFT uses the PD $\rho_2$ as basic quantity. Again unlike DFT, it does not need a (non-interacting) reference system, but it needs an approximation for $\hat{T}[\rho_2]$, from which follows the functional $E_{\text{PDFT}}[\rho_2]$. Its minimization together with an ansatz for $\rho_2$ in terms of geminals should yield $\rho_2$ and $E$ for both finite and extended systems (but not $\gamma_1$ and in the case of solids not the band structure) [87]. Another method, which uses also two-particle states (what involves the extension of LDA from densities to PDs), is in Ref.[3b], p. 325 and refs. therein.

(f) For the RDM theory in general cf. [5, 6, 7, 8]. For the investigation of the $N$-representability in terms of Kummer variety, Coleman’s algorithm, and linear inequalities cf. Ref.[8]. Whether this way is really cheaper than a full CI calculation and whether it applies to extended systems has to be checked.

(g) The generation of higher-order RDMs from $\gamma_2$ via ‘reconstruction’ has been developed by Nakatsuji, Valdemoro, and Mazziotti [7], p. 85, 117, and 139, respectively, and refs. therein, cf. also [35, 36, 37]. The philosophy behind this approach is: Let us use an exact functional and violate slightly $N$-representability rather than using approximate DFT functionals. One may criticize this attitude with the argument: Already a slight violation of the $N$-representability opens regions of the variational space, where the calculated energy is below the GS energy [38]. There seem to be encouraging results: using the positivity condition on the 2-matrix (as a necessary condition of the $N$-representability), energies of closed- and open-shell atoms and molecules were calculated variationally [36] and energies of atoms and molecules (both near and far from equilibrium geometries) were calculated solving the 1,3-CSE [37]. But critical discussions concern ‘how the results change, when going from minimal to extended basis sets?’ and ‘are the 3- and/or 4-cumulants really negligible?’ [38, 39, 40]. Whether the CSE method (provided that it survives these criticisms) applies also to extended systems has to be checked.

(h) In the Kimball-Overhauser approach [41] the singlet PD $g_+(r)$ and triplet PD $g_-(r)$ of the HEG (here normalized as $g_\pm(\infty) = 1$) are parametrized in terms of geminals
\( R_l(r, k) \), which are intuitively solutions of
\[
\left[ -\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{r^2} + \frac{1}{r} + v_{\text{sc}}^\pm(r) - k^2 \right] R_l(r, k) = 0, \tag{26}
\]
such that \( g(r) = \frac{1}{4} \left[ g_+(r) + 3g_-(r) \right] \) with
\[
g_{\pm}(r) = 2 \sum_{L}^{\pm} \frac{2}{N} \sum_{k} \mu(k) R^2_l(r, k), \quad \mu(k) = \frac{2}{N} \sum_{K} n(k_1)n(k_2), \tag{27}
\]
where \( k_1 = \frac{1}{2}K + k, k_2 = \frac{1}{2}K - k \), \( L = (l, m) \), + is for even \( l \) and − for odd \( l \). \( v_{\text{sc}}^\pm(r) \) describes the effective screening of the Coulomb repulsion by the Fermi-Coulomb hole around each electron; on the Hartree level it follows from \( \Delta v_{\text{sc}}^\pm(r) = 4\pi \rho[1 - g(r)] \). The \( R_l \) are scattering states, characterized by scattering phase shifts. In Ref. [43] the normalization and contraction SRs of the 2-matrix is related to these phase shifts. According to these new SRs it should be possible to calculate not only the PD from \( v_{\text{sc}}(r) \), but also the momentum distribution \( n(k) \). For further details cf. [41, 42, 43] and refs. therein. - Can Eq. (26) be derived from MB theory (CSE, contraction SRs, Bethe-Salpeter equation or other methods)? - To what extent is the Kimball-Overhauser approach related to the PDFT (e) and to the 2-body cluster expansion of Ref. [88]? - Whether this method correspondingly modified applies also to inhomogeneous and also to finite systems has to be studied. - A general remark of E.R. Davidson is “Scientists have not yet learned to think in terms of \( (\frac{N}{2}) \) geminals rather than in \( N \) orbitals” [5], p. 97.

(i) The Green’s function based QPT (like the KS-DFT) rests upon an effective 1-body Schrödinger equation with the local, real and energy independent XC potential \( v_{\text{XC}}(1) \) of the KS equation replaced by the non-local, complex and energy dependent XC part \( \Sigma_{\text{XC}}(1|1', \varepsilon) \) of the self-energy \([26]\). There holds an integral relation between \( v_{\text{XC}} \) and \( \Sigma_{\text{XC}} \) \([89]\, \text{Eq.}(11) \). QPT needs an approximation for the \( \Sigma_{\text{XC}} \) (e.g. the GW approximation and its vertex correction) and yields the GS properties \( \gamma_1 \) and \( E \) and besides the quasi-particle band structure \( \varepsilon_k \). Total energies were calculated \([17, \text{p. 85}] \) with the Galitskii-Migdal formula \([90]\) and with the Luttinger-Ward formula \([91]\). The real part of \( \Sigma_{\text{XC}} \) compensates (in the case of semiconductors) for the otherwise
(namely within DFT) underestimated band gaps and yields mass renormalizations. The imaginary part of $\Sigma_{\text{XC}}$ accounts for life-time effects. The Coulomb interaction between electrons in the conduction band and holes in the valence band are included by solving the Bethe-Salpeter equation for the electron-hole two-particle Green’s function \[92\]. This provides the excitonic binding energies \[93\]. The combination with the afore already mentioned dynamical mean field theory allows the first-principle approach to strongly correlated systems (Sec. VI(c), Appendix) \[94, 95\].

VII. SUMMARY

Summarizing and focusing on solids, there are several methods to calculate such GS properties as $E, \rho_1, \gamma_1$, but from a conceptional point of view only QPT Sec.VI(i) and the incremental method VI(a) yield also the band structure including Fermi surfaces (of metals) and band gaps (of semiconductors) and effective masses. So far a weak point is the PD $\rho_2$, cf. Sec.VI(e)-(h). This weakness can be removed, if the cumulant 2-matrix $\chi_2$ is calculated. This is a key quantity because from it follows: the 1-matrix $\gamma_1$ (which contains the density $\rho_1$) and using this result, the 2-matrix (which contains the PD). This PD is needed to calculate the interaction energy and particle number fluctuations in parts of the system (the magnitude of which measures the correlation strength). The spectral resolution of $\chi_2$ leads to geminals, which may be the solutions of a 2-body Schrödinger equation with a screened Coulomb interaction if not exact, but possibly to a good approximation. What peculiarities has this screening potential for different types of solids like sp metals, transition metals, semiconductors/insulators, superconductors, ferro/antiferro-magnets, strongly correlated systems? Further work is called for to answer the questions posed in this paper.

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APPENDIX: CORRELATION STRENGTH AND STRONG CORRELATION

The strength of correlation is not a matter of the correlation energy. More relevant is the quantum-kinematics expressed in terms RDs and RDMs. So the Löwdin parameter $c_2$ is one correlation index, cf. Eq. (5). Electron-number fluctuations $\Delta N_X$ in a part $X$ of the system are another index, decreasing with increasing correlation, i.e. correlation suppresses such particle-number fluctuations [1, 23], it thus favors electron localization and non-metallic behavior. The Calogero-Sutherland model shows that $\Delta N_X$ is more sensitive, because it distinguishes between attractive and repulsive interaction, whereas $c_2$ shows practically no change when changing the sign of the interaction (the non-idempotency of the momentum distribution is qualitatively the same for these two cases) [47].

Cases of strong correlation have to be described by MR states, cf. the discussion after Eq. (8). This strong-correlation case is associated with a strong suppression of fluctuations or equivalently with strong localization, cf. discussion after Eq. (6). Examples are: (i) He($Z$) for $Z > Z_{cr} = 0.91$, where one electron is localized at the nucleus while the other one becomes unbound and escapes [52], (ii) the $\text{H}_2(R)$ molecule in the dissociation limit $R \to \infty$, where at each nucleus one electron is localized such that the total spin state is a singlet [53], (iii) the Wigner crystallization of the low-density electron gas. For the case of ‘strictly correlated’ systems cf. [96]. Ferro- and antiferro-magnetism and corresponding quantum phase transitions are ‘old’ strong-correlation phenomena. ‘More new’ examples are:

- Mott insulators, where the hopping between the lattice sites is suppressed by a large Hubbard $U$: CuO, NiO, CoO [97], FeO, MnO, CaCuO$_2$, V$_2$O$_3$, Ca$_2$RuO$_4$, La$_2$CuO$_4$. Examples for correlation-driven metal-insulator transitions are FeSi (under doping), LaCoO$_3$ (under temperature), V$_2$O$_3$ and Ca$_2$RuO$_4$ (under pressure).

- Charge ordering in Yb$_4$As$_3$ or NaV$_2$O$_5$, charge-density-wave transition in CuV$_2$S$_4$,
spin-density waves in Ce(Ru$_{1-x}$Rh$_x$)$_2$Si$_2$, charge-spin separation in SiCuO$_2$, Yb$_4$As$_3$
(the thereby appearing low-lying excitations are not quasiparticles, but collective spin
and charge density fluctuations).

- Quasi-one-dimensional systems: charge-spin separation in polyacetylen (solitons) or
  in Bechgaard salts (heat transport) \cite{98}, spin-Peierls transition in CuGeO$_3$, non-Fermi
  liquid behavior in organic conductors.

- High $T_c$ superconductors and other unconventional superconductors [Sr$_2$RuO$_4$,
  ScCu(BO$_3$)$_2$]. UGe$_2$, URhGe are superconducting ferromagnets \cite{99}.

- Below characteristic temperatures heavy-fermion systems (mostly compounds of light
  lanthanoides and actinides with their 4f and 5f electrons) show anomalously large elec-
  tronic heat capacities, which can be described as heavily renormalized quasiparticles.
  They have huge effective masses being several hundred times the free-electron mass.
  Examples are (P. Fulde, in \cite{3b}, p. 111): CeAl$_3$, CeCu$_2$Si$_2$, and CeCoIn$_5$ (Kondo
  effect), Nd$_{2-x}$Ce$_x$CuO$_4$ (Zeeman effect), CeCu$_{6-x}$Au$_x$; 4f holes (respectively spin exi-
  tations) are decisive for Yb$_4$As$_3$ and 3d electrons for YMn$_2$, LiV$_2$O$_4$. The compounds
  UPd$_2$Al$_3$ and UPt$_3$ are characterized by a combined coherence of localized and itin-
  erant electrons [the 5f electrons are partially localized as in the sandwich molecule
  U(C$_8$H$_8$)$_2$], they are described by a dual model of localized and hybridized 5f elec-
  trons. The compounds CeCu$_2$Si$_2$, UBe$_{13}$, UPd$_2$Al$_3$, UPt$_3$, CeIn$_3$ are superconductors,
  ZrZn$_2$ is a superconducting ferromagnet \cite{100}. The compounds CeMn$_5$ (M=Co, Rh,
  Ir) are antiferromagnets. The compounds YbRh$_2$Si$_2$ and YbRh$_2$(Si$_{0.95}$Ge$_{0.05}$)$_2$
  have small antiferromagnetic ordering temperatures at 70 mK and 20 mK, respectively,
  and show other peculiar low-temperature behavior \cite{101}.

- Quantum criticality near $T = 0$ (where quantum fluctuations predominate thermal
  fluctuations) in CeCu$_{6-x}$Au$_x$, YMn$_2$, CePd$_2$Si$_2$, CoCu$_2$Si$_2$Ge$_3$.

Other aspects are: mixed valence compounds (SmS, Yb$_4$As$_3$), geometrical frustration
(LiV$_2$O$_4$), frustrated spin systems, non-Fermi liquid behavior (MnSi, CeCu$_2$Si$_2$, UPd$_2$Al$_3$,
YbRh$_2$Si$_2$, SrRuO$_3$ is a non-Fermi liquid ferromagnet, fractionally charged excitations in the fractional quantum Hall effect with its composite fermions (electrons+flux lines), ‘fractional charges’ (topological excitations of special low-temperature phases, possibly in LiV$_2$O$_4$). For reviews on strong electron correlation cf. Ref. [17]. Theoretical treatments (ab-initio or with models) are mentioned in Sec.VI(c),(i).

For solids, the bandwidth $W$ is compared with the Hubbard $U$, then addressing $W \gg U$ as weak and $W \lesssim U$ as strong correlation with $W \ll U$ as the atomic limit. Question: How are $c^2, \Delta N_X$, static/dynamic correlation, $W \gtrless U$ mutually related?

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