Combination of large and small basis sets in electronic structure calculations on large systems

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Two basis sets—a large and a small one—are associated with each nucleus of the system. Each atom has its own separate one-electron basis comprising the large basis set of the atom in question and the small basis sets for the partner atoms in the complex. The PATMOS model (Perturbed AToms in MOlecules and Solids) is at core of the approach since it allows for the definition of perturbed atoms in a system. It is argued that this basis set approach should be particularly useful for periodic systems. Test calculations are performed on one-dimensional arrays of H and Li atoms. The ground-state energy per atom in the linear H array, is determined versus bond length.

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I. INTRODUCTION

Standard computational models in the study of the electronic structure of molecules and solids, are formulated within the framework of one-electron basis sets. The quality of the one-electron basis determines the overall accuracy which can be obtained by a chosen computational model. For non-linear molecules, due to the simplicity in the calculation of three- and four-centre two-electron integrals, the Gaussian type functions (GTFs) are usually the preferred type of basis sets. If m is the size of the one-electron basis, the number of two-electron integrals required, scales as m^4, and the transformation of the two-electron integrals to a molecular one-electron basis, scales as m^5. The coupled-cluster model, CCSD(T) is widely used for calculation of the electron correlation energy. The computational cost of the model scales as $n_{\rm occ}^3 n_{\rm virt}^4$ where $n_{\rm occ}$ and $n_{\rm virt}$ are respectively the number of occupied and virtual orbitals. Since $n_{\rm occ}$ is proportional to m, and if the whole virtual space is adopted the overall scaling of the model is m^7. However, since the pioneering work by Pulay[1] and Sæbø and Pulay[2–5], a huge amount of work has been directed towards defining truncated virtual spaces in the coupled-cluster hierarchy of computational models. As a result, the computational feasibility of the models has been drastically improved. The very recent work by Nagy and Kállay[6] demonstrates this point. Nevertheless, the dilemma related to contradictory requirements of accuracy and computational efficiency remains: high accuracy requires a large m while computational efficiency a smaller m. This dilemma is in particular difficult for large molecules.

Our approach to partly circumvent this difficult dilemma is based on a well-known observation: in a molecular complex the dominant part of the electron density is located in the near regions of the nuclei. Accordingly, if we can identify an entity like a perturbed atom in a molecule, we can "custom-design" basis sets for each atom in the system. The basis set for an atom should be very accurate in the near region of the corresponding nucleus and less accurate in the outer regions of the nucleus. One way of identifying perturbed atoms in a complex is the PATMOS model (Perturbed AToms in MOlecules and Solids) introduced by Røeggen and Gao[7]. This model is therefore the theoretical framework of our approach. It allows for accurate, but shorter one-electron basis sets at the expense of different basis sets for different atoms. Furthermore, in our approach there is a straightforward way of defining truncated virtual spaces for calculations of the electron correlation energy.

Our basis set approach has some similarity with the dual-basis technique used in quantum chemistry[8–13]. In these techniques a small basis set is adopted for the Hartree-Fock calculation and the larger basis set is used for the electron correlation calculation. Our approach is different since we are using the same combination of small and large basis sets for both the Hartree-Fock and the correlation calculations. Hence, in order not to confuse, our basis set approach with the standard dual-basis techniques, we shall tentatively denote our approach the PATMOS basis set procedure. However, we would like to emphasize that the PATMOS model can of course also be used with regular basis sets. The PATMOS basis set approach is an additional feature of the model.

The structure of the article is as follows: Section II is devoted to a short description of the PATMOS model. Section III includes the key ideas concerning the atom-adapted basis sets, a strategy for optimizing the unrestricted Hartree-Fock wave function, and prcedures for constructing truncated virtual spaces. Section IV is focussed on periodic systems. The basis set problem is in particular difficult for this type systems due to the frequent occurrence of linear dependency when basis sets are expanded. In Section V we present some test calculations on one-dimensional periodic systems: arrays of hydrogen atoms and lithium atoms.

II. THE PATMOS MODEL

The PATMOS model[7] is based on four basic assumptions. First, the root function is an unrestricted Hartree-Fock (UHF) wave function. Second, localized orbitals are determined by the Edmiston-Ruedenberg localization scheme. Third, a minimal distortion principle is adopted for defining atoms (or ions) in complex. Fourth, the total energy is calculated according to an energy incremental scheme.

A. The perturbed atom

Let $\{\psi_i^\alpha; 1 \leq i \leq N_\alpha\}$ and $\left\{\psi_i^\beta; 1 \leq i \leq N_\beta\right\}$ denote respectively the spatial parts of the $\alpha-$ and β-type orbitals of the UHF wave function, i.e.

$$\Psi^{\mathrm{UHF}} = \det\left\{\psi_1^\alpha\alpha\cdots\psi_{N_\alpha}^\alpha\alpha\psi_1^\beta\beta\cdots\psi_{N_\beta}^\beta\beta\right\}. \tag{1}$$

According to the Edmiston-Ruedenberg procedure[14], the localized orbitals are obtained by minimizing the following functionals,

$$E^{\alpha}_{\rm Coul} = \sum_{i<j}^{N_\alpha} \left[\psi^\alpha_i \psi^\alpha_i | \, \psi^\alpha_j \psi^\alpha_j \right], \tag{2}$$

and

$$E^{\beta}_{\rm Coul} = \sum_{i<j}^{N_\beta} \left[\psi^\beta_i \psi^\beta_i \Big| \, \psi^\beta_j \psi^\beta_j \right], \tag{3}$$

by unitary transformations of the orbitals involved. In Eqs. (2)-(3) the Mulliken notation is adopted for the two-electron integrals.

In order to define perturbed atoms in the complex, we introduce the intra-atomic part of the UHF energy:

$$\begin{aligned} E^{\rm UHF}_{\rm intra} = \sum_{A=1}^{N_{\rm atoms}} \Bigg\{ & \sum_{i=1}^{N^A_\alpha} \langle \psi^{A;\alpha}_i | \mathbf{h}_A \psi^{A;\alpha}_i \rangle + \sum_{i=1}^{N^A_\beta} \langle \psi^{A;\beta}_i | \mathbf{h}_A \psi^{A;\beta}_i \rangle \\ & + \sum_{i<j}^{N^A_\alpha} \left(\left[\psi^{A;\alpha}_i \psi^{A;\alpha}_i \Big| \, \psi^{A;\alpha}_j \psi^{A;\alpha}_j \right] - \left[\psi^{A;\alpha}_i \psi^{A;\alpha}_j \Big| \, \psi^{A;\alpha}_i \psi^{A;\alpha}_j \right] \right) \\ & + \sum_{i<j}^{N^A_\beta} \left(\left[\psi^{A;\beta}_i \psi^{A;\beta}_i \Big| \, \psi^{A;\beta}_j \psi^{A;\beta}_j \right] - \left[\psi^{A;\beta}_i \psi^{A;\beta}_j \Big| \, \psi^{A;\beta}_i \psi^{A;\beta}_j \right] \right) \\ & + \sum_{i=1}^{N^A_\alpha} \sum_{j=1}^{N^A_\beta} \left[\psi^{A;\alpha}_i \psi^{A;\alpha}_i \Big| \, \psi^{A;\beta}_j \psi^{A;\beta}_j \right] \Bigg\}, \end{aligned} \tag{4}$$

where $\mathbf{h}_A$ is the one-electron Hamiltonian associated with nucleus A, charge Z_A, and nuclear position $\boldsymbol{R}_A$, i.e.

$$\mathbf{h}_A(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 - \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}|}. \tag{5}$$

The orbitals $\left\{ \psi^{A;\alpha}_i; 1 \le i \le N^A_\alpha \right\}$ and $\left\{ \psi^{A;\beta}_i; 1 \le i \le N^A_\beta \right\}$ are the localized spatial parts of the spin orbitals associated with the nucleus A.

The perturbed atom is then obtained by minimizing the functional $E^{\rm UHF}_{\rm intra}$ with respect to all possible distributions of the orbitals with respect to the nuclei. In practice only a small fraction of the distributions is required. Core orbitals are put in place straightaway, and only a small set of interchange among the "nearest neighbor" valence orbitals is needed. The optimal distribution is the one which has the lowest value of $E^{\rm UHF}_{\rm intra}$. A perturbed atom is then a nucleus and a set of electrons represented in the wave function by a set of spin

orbitals, i.e. a set of α-type orbitals and/or a set of β-type orbitals. The number of spin orbitals, i.e. $N_\alpha^A + N_\beta^A$, determines whether the perturbed atom is a neutral entity or an ion.

B. The correlation energy

The orbital energy incremental scheme was introduced in quantum chemistry by Nesbet[15]. In Nesbet approach, the correlation energy is a sum of one-electron corrections, two-electron corrections, three-electron corrections, and so on. For an N-electron system with UHF wave function

$$\Psi^{\mathrm{UHF}} = \det\left\{\psi_1\psi_2\cdots\psi_N\right\}, \tag{6}$$

and where $\{\psi_i; 1 \le i \le N\}$ are the occupied spin orbitals, the correlation energy is written as

$$\epsilon^{\mathrm{corr}} = \sum_{i=1}^{N}\epsilon_i + \sum_{i<j}^{N}\epsilon_{ij} + \sum_{i<j<k}^{N}\epsilon_{ijk} + \cdots. \tag{7}$$

The energy corrections are obtained by partial full configuration interaction (FCI) calculations. Nesbet's original work has been refined by Stoll and co-workers[16–18], by Røeggen[19,20] and more recently by Bytautas and Ruedenberg[21]. A multireference incremental scheme has been introduced by Voloshina and Paulus[22] in a correlation treatment of bulk metals.

In this work we generalize the Nesbet approach by considering the perturbed atom as the basic unit. The UHF wave function is written as

$$\Psi^{\mathrm{UHF}} = \det\left\{\prod_{A=1}^{N_{\mathrm{atoms}}}\left(\psi_1^A\cdots\psi_{N_A}^A\right)\right\}, \tag{8}$$

where $\{\psi_i^A; i = 1,\cdots,N_A\}$ are the spin orbitals of atom A. The correlation energy is then a sum of intra- and inter-atomic corrections:

$$E^{\mathrm{corr}} = \sum_{A=1}^{N_{\mathrm{atoms}}}E_A^{\mathrm{corr}} + \sum_{A<B}^{N_{\mathrm{atoms}}}E_{AB}^{\mathrm{corr}} + \sum_{A<B<C}^{N_{\mathrm{atoms}}}E_{ABC}^{\mathrm{corr}} + \cdots. \tag{9}$$

The correlation terms in Eq. (9) are calculated by a size extensive correlation model (CM), for example FCI, a Nesbet hierarchy of orbital corrections or a coupled-cluster model. For atom A we have an effective Hamiltonian:

$$\mathbf{H}_{\mathrm{eff}}^A = \sum_{i=1}^{N_A}\mathbf{h}_{\mathrm{eff}}^A(\boldsymbol{r}_i) + \sum_{i<j}^{N_A}\frac{1}{r_{ij}}. \tag{10}$$

The effective one-electron Hamiltonian is given by

$$\mathbf{h}^A_{\rm eff}(\boldsymbol{r}_i) = \mathbf{h}(\boldsymbol{r}_i) + \sum_{B\neq A}^{N_{\rm atoms}} \sum_{j=1}^{N_B} (J_j^B - K_j^B). \tag{11}$$

If only Coulomb interaction are included,

$$\mathbf{h}(\boldsymbol{r}_i) = -\frac{1}{2}\nabla_i^2 - \sum_{B=1}^{N_{\rm atoms}} \frac{Z_B}{|\boldsymbol{R}_B - \boldsymbol{r}_i|}. \tag{12}$$

In Eq. (11), J_j^B and K_j^B are, respectively, Coulomb and exchange operators defined by the spin orbital ψ_j^B. The intra-atomic correlation energy is then calculated as follows:

$$\mathbf{H}^A_{\rm eff}\Psi^{\rm CM}_A = \lambda^{\rm CM}_A \Psi^{\rm CM}_A, \tag{13}$$

$$E^{\rm UHF}_A = \langle \Psi^{\rm UHF}_A | \mathbf{H}^A_{\rm eff} \Psi^{\rm UHF}_A \rangle, \tag{14}$$

$$E^{\rm CM}_A = \lambda^{\rm CM}_A - E^{\rm UHF}_A. \tag{15}$$

The energy eigenvalue equation Eq. (13) is solved by means of the chosen correlation model, and $\Psi^{\rm UHF}_A$ is the UHF wave function defined by the spin orbitals $\left\{\psi_i^A; 1 \le i \le N^A\right\}$. If CM is the FCI model, then

$$E^{\rm CM}_A = E^{\rm corr}_A. \tag{16}$$

Otherwise, $E^{\rm CM}_A$ is an approximation to $E^{\rm corr}_A$.

The diatomic correlation terms are determined by a similar set of equations:

$$\mathbf{H}^{AB}_{\rm eff}\Psi^{\rm CM}_{AB} = \lambda^{\rm CM}_{AB} \Psi^{\rm CM}_{AB}, \tag{17}$$

$$E^{\rm UHF}_{AB} = \langle \Psi^{\rm UHF}_{AB} | \mathbf{H}^{AB}_{\rm eff} \Psi^{\rm UHF}_{AB} \rangle, \tag{18}$$

$$E^{\rm CM}_{AB} = \lambda^{\rm CM}_{AB} - E^{\rm UHF}_{AB} - E^{\rm CM}_A - E^{\rm CM}_B. \tag{19}$$

The definitions of the symbols in Eqs. (17)–(19) are obtained by straightforward modifications of Eqs. (10)–(12). Furthermore, three-atomic and higher order corrections can be generated in a similar way.

III. ATOM-ADAPTED BASIS SETS

A localized orbital associated with a perturbed atom is most appropriately described by a large atom-centered basis set on the nucleus in question and smaller basis sets on the

partner nuclei of this particular atom. Hence, in this novel approach we specify two different atom-centered basis sets for each nucleus: a small basis set, $\left\{\chi_\mu^{A,sb}; \mu = 1, \cdots, m_A^{sb}\right\}$, and a large basis set, $\left\{\chi_\mu^{A,lb}; \mu = 1, \cdots, m_A^{lb}\right\}$. The basis set for atom A is then

$$\begin{aligned}\Omega_{\rm dual}^A &= \left\{\chi_\mu^{A,{\rm dual}}; \mu = 1, \cdots, m_A^{\rm dual}\right\} \\ &= \left\{\chi_\mu^{A,lb}; \mu = 1, \cdots, m_A^{lb}\right\} \bigcup_{B\neq A}^{N_{\rm atoms}} \left\{\chi_\mu^{B,sb}; \mu = 1, \cdots, m_B^{sb}\right\}. \end{aligned} \tag{20}$$

The spatial part of a spin orbital (α- or β-type)

$$\psi_i^A = \sum_{\mu=1}^{m_A^{\rm dual}} U_{\mu,i}^{\rm dual} \chi_\mu^{A,{\rm dual}}. \tag{21}$$

The orbitals of the UHF wave functions are subjected to orthogonality constraints:

$$\langle \psi_i^{A,\alpha} | \psi_j^{B,\alpha} \rangle = \delta_{ij}\delta_{AB}, \tag{22}$$

$$\langle \psi_i^{A,\beta} | \psi_j^{B,\beta} \rangle = \delta_{ij}\delta_{AB}. \tag{23}$$

Since we have different basis sets for different atoms, these constraints require special attention in the optimization of the UHF wave function.

A. Optimization of the UHF function

The optimization of the UHF function is a two-step procedure. In step one we calculate the UHF function for the complex using a small basis set for all atoms. We then localize the spin orbitals and define the atoms (ions).

For the periodic systems we use a simplified localization scheme. The orbitals of the atoms of the reference unit cell are at each step of the iterative sequence localized by maximizing the overlap with the orbitals of the isolated atoms, i.e. we use the minimal distortion localization scheme introduced by Ahmadi and Røeggen[23]. By this procedure the atoms are in a sense predefined. For cases involving electron transfer, we will have atoms with dipole character.

In step two we start with the localized orbitals in step one, as start orbitals. The orbitals satisfy the orthogonality requirement expressed by Eqs. (22)–(23). Then we proceed through a set of iterative cycles. In each cycle the UHF wave function for each atom is calculated. The UHF equations are solved in an orbital space orthogonal to the occupied orbtials of

the partner atoms. Let $P_{\rm occ}^{B,\alpha}$ denote the projection operator defined by the occupied α-type orbtials of atom B. The dual space $\Omega_{\rm dual}^{A}$, Eq. (20), is modified:

$$\hat{\chi}_{\mu}^{A,\rm dual} = \left(1 - \sum_{B\neq A}^{N_{\rm atoms}} P_{\rm occ}^{B,\alpha}\right) \chi_{\mu}^{A,\rm dual},\ 1 \leq \mu \leq m_A^{\rm dual}. \tag{24}$$

A linear independent set of functions, $\left\{\phi_{\mu}^{A,\alpha}; 1 \leq \mu \leq \tilde{m}_A^{\rm dual} \leq m_A^{\rm dual}\right\}$, is constructed from the set of modified functions $\left\{\hat{\chi}_{\mu}^{A,\rm dual}; 1 \leq \mu \leq m_A^{\rm dual}\right\}$. The Hartree-Fock equations for α-type orbtials are then solved within the space $\left\{\phi_{\mu}^{A,\alpha}\right\}$. A similar approach is adopted for the β-type orbitals.

If we denote the spin orbitals of the previous cycle, $\left\{\psi_i^{A,\rm old}; 1 \leq i \leq N_A; 1 \leq A \leq N_{\rm atoms}\right\}$, and the spin orbitals of the present cycle, $\left\{\psi_i^{A,\rm new}; 1 \leq i \leq N_A; 1 \leq A \leq N_{\rm atoms}\right\}$, we have by construction:

$$\langle \psi_i^{A,\rm new} | \psi_j^{B,\rm old} \rangle = 0,\ B \neq A, 1 \leq i \leq N_A, 1 \leq j \leq N_B. \tag{25}$$

However, $\langle \psi_i^{A,\rm new} | \psi_j^{B,\rm new} \rangle$, is not strictly zero when $B \neq A$. Hence, we modify the new orbitals in order to come closer to the orthogonality condition. We introduce orbital corrections

$$\Delta\psi_i^A = \psi_i^{A,\rm new} - \psi_i^{A,\rm old}, \tag{26}$$

and modified orbitals

$$\hat{\psi}_i^{A,\rm mod} = \psi_i^{A,\rm old} + \lambda \Delta\psi_i^A,\ 1 \leq i \leq N_A, 1 \leq A \leq N_{\rm atoms}. \tag{27}$$

In Eq. (27) λ is a parameter in the range $0 < \lambda \leq 1$ For each atom we perform a symmetric orthonormalization of the spin orbitals $\left\{\hat{\psi}_i^{A,\rm mod}; 1 \leq i \leq N_A\right\}$, i.e. $\left\{\hat{\psi}_i^{A,\rm mod}\right\} \rightarrow \left\{\psi_i^{A,\rm mod}\right\}$, such that

$$\langle \psi_i^{A,\rm mod} | \psi_j^{A,\rm mod} \rangle = \delta_{ij}, 1 \leq i,j \leq N_A, 1 \leq A \leq N_{\rm atoms.} \tag{28}$$

Then we define an overlap functional:

$$L(\lambda) = \sum_{A<B}^{N_{\rm atoms}} \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} |\langle \psi_i^{A,\rm mod} | \psi_j^{B,\rm mod} \rangle|^2. \tag{29}$$

By minimizing $L(\lambda)$ we obtain orbitals which are more in accordance with the orthogonality constraints. In the end of the iteration procedure, the orthogonality constraints are strictly fulfilled due to Eq. (25).

B. Truncated virtual orbital spaces

The use of truncated but efficient, virtual orbital spaces for electron correlation calculations, is of paramount importance. In the pioneering works by Pulay[1] and Pulay and Sæbø[2–5], there is a truncated virtual space for each pair of occupied orbitals. In this work the truncation of virtual space is closely related to the incremental scheme adopted for the calculation of the electron correlation energy.

The occupied orbitals of atom A are expressed in terms of the basis $\Omega^A_{\rm dual}$, i.e. Eq. (20). Since the occupied orbitals are localized in a region close to the nucleus of atom A, an efficient truncated virtual orbital space for the intra-atomic corelation energy, can be obtained from a proper modification of the large basis set $\left\{\chi^{A,lb}_\mu; 1 \le \mu \le m^{lb}_A\right\}$. The modification is due to orthogonality constraints. All virtual orbitals must be orthogonal to all occupied orbitals of the system. Let us first consider the virtual space of α-type orbitals. An auxilliary virtual space is constructed from $\Omega^A_{\rm dual}$:

$$\chi^{A,\rm aux}_\mu = \left(1 - \sum_{B=1}^{N_{\rm atoms}} P^{B,\alpha}_{\rm occ}\right) \chi^{A,\rm dual}_\mu,\ 1 \le \mu \le m^{\rm dual}_A. \tag{30}$$

In Eq. (30) $P^{B,\alpha}_{\rm occ}$ denotes the projection operator defined by the occupied α-type orbitals of atom B, and $\chi^{A,\rm dual}_\mu \in \Omega^A_{\rm dual}$. Let $P^{A,\rm aux}_{\rm virt}$ denote the projection operator associated with the auxilliary space $\left\{\chi^{A,\rm aux}_\mu; 1 \le \mu \le m^{\rm dual}_A\right\}$. In the next step we project the basis functions $\left\{\chi^{A,lb}_\mu; 1 \le \mu \le m^{lb}_A\right\}$ onto this auxilliary space:

$$\hat{\chi}^{A,lb}_\mu = P^{A,\rm aux}_{\rm virt} \chi^{A,lb}_\mu,\ 1 \le \mu \le m^{lb}_A. \tag{31}$$

The functions $\left\{\hat{\chi}^{A,lb}_\mu; 1 \le \mu \le m^{lb}_A\right\}$ satisfy the orthogonality constraints by construction. Then we diagonalize the overlap matrix $(\langle\hat{\chi}^{A,lb}_\mu|\hat{\chi}^{A,lb}_\nu\rangle)$ and select the eigenfunctions corresponding to the $(m^{lb}_A - N^A_\alpha)$ largest eigenvalues.

The proper truncated virtual space for atom A is then obtained by some appropriate matrix multiplications defined by the preceding steps. Since we have the same number of virtual orbitals as for an isolated atom, there is no basis set superposition error at the correlation level in this computational scheme. We would also like to stress that the use of the auxilliary virtual space is important in order to have a truncated virtual space which is not too much distorted by the occupied orbitals of the partner atoms.

The construction of the truncated virtual spaces for the diatomic correlations follows a similar procedure as for the intra-atomic case. For the cluster (A, B) we have a dual space:

$$\begin{aligned}\Omega^{AB}_{\rm dual} &= \left\{\chi^{AB,{\rm dual}}_{\mu}; 1 \leq \mu \leq m^{\rm dual}_{AB}\right\} \\ &= \left\{\chi^{A,lb}_{\mu}; 1 \leq \mu \leq m^{lb}_{A}\right\} \bigcup \left\{\chi^{B,lb}_{\mu}; 1 \leq \mu \leq m^{lb}_{B}\right\} \bigcup_{C \neq A,B}^{N_{\rm atoms}} \left\{\chi^{C,sb}_{\mu}; 1 \leq \mu \leq m^{sb}_{C}\right\}. \end{aligned} \tag{32}$$

An auxilliary space for α-type orbitals is defined by

$$\chi^{AB,{\rm aux}}_{\mu} = \left(1 - \sum_{C=1}^{N_{\rm atoms}} P^{C,\alpha}_{\rm occ}\right) \chi^{AB,{\rm dual}}_{\mu},\ 1 \leq \mu \leq m^{\rm dual}_{AB}. \tag{33}$$

Let $P^{AB,{\rm aux}}_{\rm virt}$ denote the projection operator associated with the auxilliary space $\left\{\chi^{AB,{\rm aux}}_{\mu}; 1 \leq \mu \leq m^{\rm dual}_{AB}\right\}$, and the large space for (A, B),

$$\begin{aligned}\Omega^{AB,{\rm lb}} &= \left\{\chi^{A,lb}_{\mu}; 1 \leq \mu \leq m^{lb}_{A}\right\} \bigcup \left\{\chi^{B,lb}_{\mu}; 1 \leq \mu \leq m^{lb}_{B}\right\} \\ &= \left\{\chi^{AB,lb}_{\mu}; 1 \leq \mu \leq (m^{lb}_{A} + m^{lb}_{B})\right\}. \end{aligned} \tag{34}$$

In order to satisfy the orthogonality condition, the elements of $\Omega^{AB,{\rm lb}}$ are projected onto the space of the auxilliary functions:

$$\hat{\chi}^{AB,lb}_{\mu} = P^{AB,{\rm aux}}_{\rm virt} \chi^{AB,lb}_{\mu},\ 1 \leq \mu \leq (m^{lb}_{A} + m^{lb}_{B}). \tag{35}$$

Then we diagonalize the overlap matrix $(\langle \hat{\chi}^{AB,lb}_{\mu} | \hat{\chi}^{AB,lb}_{\nu} \rangle)$ and select the $(m^{lb}_{A} + m^{lb}_{B} - N^{A}_{\alpha} - N^{B}_{\alpha})$ eigenvectors associated with the largest eigenalues. By a trivial transformation of the orbitals we arrive at the proper truncated virtual space for α-type orbitals of the diatomic cluster (A, B).

It remains to be said that the virtual β-type orbitals are obtained by similar procedures. The extension to three-atom truncated virtual spaces is of course straightforward. Furthermore, basis set superposition error is of concern, then the intra-atomic corrections to be used in Eq. (19), should be recalculated with the dimer virtual spaces as virtual spaces.

IV. PERIODIC SYSTEMS

As stated in the Section I, the basis set problem is in particular difficult for periodic systems. Our approach on large systems is slightly modified when we are dealing with this type of system.

An infinite system of periodic unit cells is approximated by a finite set of identical unit cells where $N^{\rm uc}_{\rm model}$ is the number of unit cells in the model. Further, we define a basis function (BF) region as a unit cell and a certain number of nearest neighbor unit cells. The number of unit cells included in the BF-region is denoted $N^{\rm uc}_{\rm bf}$. See illustration in Fig. 1. The basis set for an atom in the reference cell is then

$$\{\chi^{A,lb}_{\mu}; 1 \leq \mu \leq m^{lb}_{A}\} \bigcup_{B \neq A}^{\text{BF-region}} \{\chi^{B,sb}_{\mu}; 1 \leq \mu \leq m^{sb}_{B}\}. \tag{36}$$

As shown by Røeggen and Gao[7], the PATMOS energy can be partitioned in the following way:

$$E^{\rm PATMOS} = \sum_{A=1}^{N_{\rm atoms}} (E^{\rm UHF}_{A} + E^{\rm corr}_{A}) + \sum_{A<B}^{N_{\rm atoms}} (E^{\rm Coul}_{AB} + E^{\rm exch}_{AB} + E^{\rm corr}_{AB}) + \sum_{A<B<C}^{N_{\rm atoms}} E^{\rm corr}_{ABC} + \cdots . \tag{37}$$

In Eq. (37) $E^{\rm Coul}_{AB}$ and $E^{\rm exch}_{AB}$ are respectively the Coulomb and exchange part of the interaction energy between the atoms A and B. Effective atomic energies can be introduced:

$$E^{\rm PATMOS} = \sum_{A=1}^{N_{\rm atoms}} E^{\rm eff}_{A}, \tag{38}$$

where

$$\begin{aligned} E^{\rm eff}_{A} = {} & E^{\rm UHF}_{A} + E^{\rm corr}_{A} + \frac{1}{2} \sum_{B \neq A}^{N_{\rm atoms}} (E^{\rm Coul}_{AB} + E^{\rm exch}_{AB} + E^{\rm corr}_{AB}) \\ & + \frac{1}{3} \left\{ \sum_{\substack{B,C \\ A<B<C}}^{N_{\rm atoms}} E^{\rm corr}_{ABC} + \sum_{\substack{B,C \\ B<A<C}}^{N_{\rm atoms}} E^{\rm corr}_{BAC} + \sum_{\substack{B,C \\ B<C<A}}^{N_{\rm atoms}} E^{\rm corr}_{BCA} \right\} + \cdots . \end{aligned} \tag{39}$$

For a periodic system, the important term is the sum of effective atomic energies for the atoms of the reference cell, i.e.

$$E^{\rm PATMOS}_{\rm uc} = \sum_{A=1}^{N^{\rm uc}_{\rm atoms}} E^{\rm eff}_{A}, \tag{40}$$

where $N^{\rm uc}_{\rm atoms}$ is the number of atoms in the unit cell. As we increase the number of unit cells in the model, i.e. $N^{\rm uc}_{\rm model}$, the term $E^{\rm PATMOS}_{\rm uc}$ should converge to the corresponding term for the infinite system.

V. TEST CALCULATIONS

To illustrate the features of the advocated basis set approach, we consider test cases on periodic systems. One-dimensional arrays of hydrogen and lithium atoms are chosen as test systems.

Our code requires family type basis sets. The procedure for constructing the basis sets is described in Appendix in the work by Røeggen and Gao[7]. The parameters defining the basis sets are given in Table I. The correlation energy is calculated according to the Nesbet scheme[15], i.e. Eq. (7). Since our work is essentially a basis set study, it is sufficient to include only the two-elctron terms in the Nesbet scheme. The two-electron correlation terms are calculated by the FCI model. Hence, the calculations scale as m_{virt}^4, where m_{virt} is the number of virtual orbitals. In this work we use an integral threshold of 10^{-7} Hartree for the Cholesky decomposition of the two-electron matrix.

A. One-dimensional array of H atoms

Our basis set of calculations is on a chain of H atoms with an equal nearest neighbor distance of $r_{\text{H1,H2}} = 2$ bohr, and hence a unit cell distance of $r_{\text{uc}} = 4$ bohr. The calculations yield an α-type orbital centered on one nucleus and a β-type orbital on the second nucleus of the unit cell. The extension of the corresponding electron densities are described by charge ellipsoids[7]. This geometrical information is displayed in Fig. 2.

Three different uncontracted GTF basis sets are chosen as small basis (sb) sets: $(10s1p)$, $(10s2p)$ and $(10s2p1d)$. Two large basis sets are adopted: an uncontracted $(13s4p3d1f)$ GTF and an uncontracted $(13s6p5d4f3g2h1i)$ GTF. The last set is an even-tempered extension of the $(13s4p3d1f)$ set. A model system with $N_{\text{model}}^{\text{uc}} = 13$ and $N_{\text{bf}}^{\text{uc}} = 13$, $(sb) = (10s2p1d)$ and $(lb) = (13s4p3d1f)$, implies that the number of basis functions for an atom is equal to 572. On the other hand, using the (lb) set on all atoms, yields 1222 basis functions. Hence the (sb/lb) combination gives a substantial reduction of the number of basis functions. It should be mentioned that for the actual geometry, and parameters $N_{\text{model}}^{\text{uc}} = N_{\text{bf}}^{\text{uc}} = 13$, a larger small basis than $(10s2p1d)$ generated linear dependency.

In Table II we present calculations of the unit cell energies at both the UHF and the PATMOS level for different values of the parameters: $N_{\text{model}}^{\text{uc}}$—the number of unit cells

included in the model, and $N_{\rm bf}^{\rm uc}$—the number of unit cells included in the basis function region. Pertaining to the results conveyed by this table, we first notice the close similarity of the UHF results for the two basis sets (sb) and (sb/lb). This is of course due to the fact that the GTF set $(10s2p1d)$ is fairly close to the basis set limit for HF calculations on the H chain. Accordingly, large basis sets are not very important at the UHF level. However, for the electron correlation part, a large basis is important. The main information presented in this table is that high accuracy requires large values for both $N_{\rm model}^{\rm uc}$ and $N_{\rm bf}^{\rm uc}$. In Table III we consider three different small basis sets. We notice that even with smallest basis, i.e. $(10s1p)$, the error is quite small. This result is important since it suggests that the advocated basis set approach works well for periodic systems.

Motta et al.[24] have very recently published an extensive study of finite chains of hydrogen atoms. A variety of many-body methods were considered. H chains with nearest neighbor distance $R \in \{1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8, 3.2, 3.6\}$ bohr were included in their report. In their work they introduced the thermodynamic limit as

$$E_{\rm TDL}(R) = \lim_{N\to\infty} E(N, R), \tag{41}$$

where $E(N, R)$ is the energy per atom for a chain with N atoms and distance R. They estimated the thermodynamic limit by extrapolation with N ranging from 10 to 102. They also use the term equation of state (EOS) to refer to $E_{\rm TDL}(R)$ versus R at zero temperature. Furthermore, they also extrapolated to the complete basis set limit. Table VI (Final equation state for the hydrogen chain at the thermodynamic limit) in Ref.[24] summarizes their results.

From Table VI of Motta et al.[24] we include the wave function based models AFQMC (Auxiliary-Field Quantum Monte Carlo), UCCSD (Coupled Cluster theory with Single and Double excitations and UHF as a reference state), and UHF (Unrestricted Hartree Fock). AFQMC is included for comparison since it is supposed to give the most accurate result, but with a somewhat large random uncertainty. UCCSD is included since it is based on UHF as a root function, as is also the case for the PATMOS models. In our Table IV we include the results for the three selected models from Motta et al.[24] together with the UHF and PATMOS results. We have also included in Table IV the results obtained by what we denote a basis set corrected PATMOS model, i.e. PATMOS$(13s4p3d1f/13s6p5d4f3g2h1i)$. This correction is based on the following observation. For the distance $R = 2.0$ bohr we have respectively correlation contribution to the energy per atom equal -0.023761 Hartree and

-0.023593 Hartree for the parameter combinations $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$ and $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 7$. Hence, in order to estimate the change in PATMOS energy by changing $(lb) = (13s4p3d1f)$ to $(lb) = (13s6p5d4f3g2h1i)$ we might just as well use the PATMOS model with the parameters $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 7$. We then calculate the energy per atom difference between PATMOS$(13s6p4d4f3g2h1i)$ and PATMOS$(13s4p3d1f)$ and add this difference to the energy per atom obtained by PATMOS$(13s4p3d1f)$ with parameters $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$. In Table IV these basis set corrected results are marked with the heading PATMOS$(13s4p3d1f/13s6p5d4f3g2h1i)$. To avoid linear dependency, threshold equal 10^{-7}, we have for the two smallest distances, $R = 1.4$ bohr and $R = 1.6$ bohr, changed the small basis from $(sb) = (10s2p1d)$ to $(sb) = (10s1p)$. Furthermore, in calculating the basis set corrections for these distances the two most diffuse s-type functions were deleted in the larger basis sets for the same reason.

Pertaining to the results presented in Table IV, we would like to emphasize the following points. First, the UHF results obtained with the (sb/lb) combination compare favourably with the converged results of Motta et al. Our (sb/lb) approach yields practically the same results as the computationally much more expensive procedure with very large basis sets required for the extrapolation to the complete basis set limit. Second, for distances $R \geq 1.6$ bohr, the PATMOS$(13s4p3d1f)$ results are closer to the AFQMC results than the results of UCCSD. By including the basis set correction, i.e. the PATMOS$(13s4p3d1f/13s6p5d4f3g2h1i)$, the agreement with AFQMC is overall better. If we compare our most accurate results, i.e. PATMOS$(13s4p3d1f/13s6p5d4f3g2h1i)$, and the results of the UCCSD model, with the AFQMC calculations, the UCCSD model has a mean absolute error of 0.00186 Hartree and a maximum absolute error of 0.00219 Hartree. The corresponding quantities for the PATMOS model are respectively 0.00074 Hartree and 0.00214 Hartree. Accordingly, the PATMOS model has a somewhat oscillatory character. This feature is not related to the model as such, but due to the adopted correlation model in this study. Truncation in the Nesbet scheme at the two-electron level, implies that all poly-electron terms are neglected. The relative error of the calculated correlation energy by this truncation is usually between 1 and 10%. The error can be either positive or negative, depending on the system and the configuration of the nuclei. An error of 5% corresponds roughly to 0.0012 Hartree per atom of the H chain. It is therefore very likely that the good agreement obtained for the distances (1.6, 2.0 and 2.8 bohr) are due to a fortuitous cancel-

lation of errors, i.e. neglected three-electron terms with different signs. For distances where there are larger discrepancies between the AFQMC and the PATMOS model, it is likely that the most important three-electron terms have the same sign. Therefore, by including three-electron terms in this type of calculations the oscillatory character of the errors will be drastically reduced.

B. One-dimensional array of Li atoms

The one-dimensional array of Li atoms has an equal nearest neighbor distance of $r_{\mathrm{Li1,Li2}} = 5.74421$ bohr, the experimental equilibrium distance of nearest neighbor atoms in bcc solid lithium[25]. As dispalyed in Fig. 3, the bonding in this system is characterized by one-electron bonds between the nuclei. Hence the perturbed atom in this case has electric dipole character.

In the calculations on the Li atoms we have one fixed small basis set: an uncontracted $(11s2p)$ GTF basis, and two large basis sets: uncontracted $(15s7p2d1f)$ GTF and $(19s8p7d5f2g1h)$ GTF. As in the hydrogen study we include only two-electron FCI calculations. Core-core correlation terms are neglected since their magnitude are less than 10^{-6} Hartree. However, core-valence correlation terms are important due to the large shift of the valence orbitals from isolated atom to perturbed atoms of the Li chain. Three-electron correlation terms can for this system be safely neglected. For the isolated Li atom the total PATMOS energy using the basis set $(19s8p7d5f2g1h)$, is respectively -7.477094 Hartree and -7.477080 Hartree with and without three-electron correlation energies (estimated nonrelativistic limit[26] for the Li energy is -7.478060 Hartree). By using the smaller of the two (lb) sets, i.e. $(15s7p2d1f)$, the PATMOS energy for the isolated atom is -7.472984 Hartree. The isolated atomic energies are obtained by performing calculation on Li with an internuclear distance equal 100.0 bohr.

In Table V we present the effective unit cell energies and correlation contributions for different values of the model parameters $N^{\mathrm{uc}}_{\mathrm{model}}$ and $N^{\mathrm{uc}}_{\mathrm{bf}}$. As for the results of this table we would like to emphasize that the energies converge nicely with the size of the model system, but more slowly than the H atom case. The slower convergence is of course due to the dipole character of the perturbed atoms. However, the correlation terms, intra- and interatomic contributions, have a somewhat faster convergence.

Energy differences, say binding energies, are important in chemistry. In Table VI we look at the energy difference between the effective unit cell energy and two isolated Li atoms. By using the two different large basis sets, we notice that the smaller of the basis sets, yields a result which is in "error" by approximately 1.5%.

To conclude, our calculations on the Li atoms demonstrate clearly that the advocated basis set approach can be used for metallic type systems if the perturbed atoms can be described by orbitals located in vicinity of the corresponding nuclei.

VI. CONCLUDING REMARKS

As emphasized in the Introduction, accurate calculations on large systems are very demanding with respect to the quality of the one-electron basis sets. We have demonstrated in this work that the adoption of a combination of large and small basis sets for the atoms involved might be a way of circumventing the dilemma between the use of large basis sets and computational feasibility. Furthermore, the results obtained for the H chain suggest that the PATMOS model works well for periodic systems, in particular if we use a more sophisticated correlation approach such as UCCSD(T) or the Nesbet scheme where the most important three-electron FCI terms are included.

Our approach is based on the assumption that it is possible to define what we call "perturbed atoms" in a system. We have not yet shown that this is always the case, even if it is highly likely. The obvious challenge is the metals. In a forthcoming work we shall report on more comprehensive studies of Li chains and lattices.

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TABLE I. Lowest exponents of the GTF-family basis sets used in this work.

Atoms/Basis	Reference basis[27]	s	p	d	f	g	h	i
H/$(10s, 1p)$	cc-pVTZ	0.144717	1.05700					
H/$(10s, 2p)$	cc-pVTZ	0.144717	0.391109					
H/$(10s, 2p, 1d)$	cc-pVTZ	0.144717	0.391109	1.057000				
H/$(13s, 4p, 3d, 1f)$	cc-pVQZ	0.035763	0.223520	0.558800	1.397000			
H/$(13s, 6p, 5d, 4f, 3g, 2h, 1i)$[a]		0.035763	0.223520	0.223520	0.558800	1.397000	3.492500	8.731250
Li/$(11s, 2p)$[b]		0.018708	0.055677					
Li/$(15s, 7p, 2d, 1f)$	cc-pVQZ	0.031055	0.031055	0.075366	0.182900			
Li/$(19s, 8p, 7d, 5f, 2g, 1h)$	cc-pV5Z	0.003801	0.054000	0.054000	0.131000	0.131000	0.320000	

[a] An even-tempered extension of the H/$(13s, 4p, 3d, 1f)$ set.

[b] Energy optimized by minimizing the energy of Li_2, $R = 5.05$ bohr, with $(11s, 2p, 1d)$ GTF-family basis.

TABLE II. Changes in effective unit cell energies as a function of model parameters for a one-dimensional array of H atoms. $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$, as reference level. Basis: $(sb/lb) = (10s2p1d/13s4p3d1f)$. Nearest neighbor distance: 2.0 bohr. Isolated atomic energy with $(13s4p3d1f)$ basis: $-0.499999\ E_h$.

$N^{\rm uc}_{\rm model}$	$N^{\rm uc}_{\rm bf}$	$\Delta E^{\rm UHF,eff}_{\rm uc}\ (sb)$ (E_h)	$\Delta E^{\rm UHF,eff}_{\rm uc}\ (sb/lb)$ (E_h)	$\Delta E^{\rm PATMOS,eff}_{\rm uc}\ (sb/lb)$ (E_h)	$\left(E^{\rm PATMOS,eff}_{\rm uc} - 2E^{\rm PATMOS}_{\rm atom}({\rm isolated})\right)/2$ (E_h)
13	3	0.015899	0.015991	0.013270	−0.056188
13	5	0.001914	0.002052	0.002522	−0.061398
13	7	0.000576	0.000595	0.000806	−0.062256
13	9	0.000207	0.000173	0.000250	−0.062535
13	11	0.000046	0.000049	0.000097	−0.062637
13	13	0.0	0.0	0.0	−0.062659
		(−1.077629)	(−1.077797)	(−1.125317)	
3	3	0.003584	0.003617	0.005048	−0.060350
5	5	0.000614	0.000636	0.001279	−0.062086
7	7	0.000111	0.000120	0.000357	−0.062502
9	9	0.000015	0.000016	0.000092	−0.062621
11	11	0.000000	0.000000	0.000019	−0.062653
13	13	0.0	0.0	0.0	−0.062659
		(−1.077629)	(−1.077797)	(−1.125317)	

TABLE III. Changes in effective unit cell energies with different basis sets for the H-atom chain. Reference basis: $(10s2p1d/13s4p3d1f)$. Model parameters: $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$. Nearest neighbor distance: 2.0 bohr.

Basis sets		$\Delta E^{\rm UHF,eff}_{\rm uc}$ (sb/lb)	$\Delta E^{\rm PATMOS,eff}_{\rm uc}$ (sb/lb)
sb	lb	(E_h)	(E_h)
$10s1p$	$13s4p3d1f$	0.000030	0.000023
$10s2p$	$13s4p3d1f$	0.000020	0.000022
$10s2p1d$	$13s4p3d1f$	0.000000	0.000000
		(-1.077797)	(-1.125317)

TABLE IV. The equation of state for the chain of H atoms calculated by different models. PATMOS and UHF with model parameters $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$. Literature data from Motta et al[24].

R	AFQMC[24]	UCCSD[24]	UHF[24]	UHF	PATMOS	PATMOS[a]
					$(13s4p3d1f)$	$(13s4p3d1f/13s6p5d4f3g2h1i)$
(bohr)	(E_h)	(E_h)	(E_h)	(E_h)	(E_h)	(E_h)
1.4	−0.54044(35)	−0.53897(22)	−0.51234(3)	−0.51202	−0.53779	−0.53830
1.6	−0.55971(36)	−0.55778(15)	−0.53256(2)	−0.53240	−0.55918	−0.55987
1.8	−0.56569(30)	−0.56354(7)	−0.53925(1)	−0.53918	−0.56366	−0.56448
2.0	−0.56444(34)	−0.56238(2)	−0.53894(1)	−0.53890	−0.56266	−0.56449
2.4	−0.55313(31)	−0.55105(2)	−0.52978(1)	−0.52976	−0.55184	−0.55253
2.8	−0.53886(29)	−0.53666(7)	−0.51883(1)	−0.51881	−0.53839	−0.53888
3.2	−0.52557(23)	−0.52403(12)	−0.51058(1)	−0.51058	−0.52620	−0.52658
3.6	−0.51611(22)	−0.51462(14)	−0.50556(1)	−0.50555	−0.51654	−0.51683

[a] Explanation in the body of the text.

TABLE V. Changes in effective unit cell energies as a function of model parameters for a one-dimensional array of Li atoms. $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 13$, as reference level. Basis: $(sb/lb) = (11s2p/15s7p2d1f)$. Nearest neighbor distance: 2.0 bohr. $E^{\rm PATMOS}_{{\rm atom},lb}$(isolated): -7.472984 E_h.

$N^{\rm uc}_{\rm model}$	$N^{\rm uc}_{\rm bf}$	$\Delta E^{\rm UHF,eff}_{\rm uc}$ (sb/lb) (E_h)	$\Delta E^{\rm intra,corr}_{\rm uc}$ (sb/lb) (E_h)	$\Delta E^{\rm inter,corr,eff}_{\rm uc}$ (sb/lb)	$\Delta E^{\rm PATMOS,eff}_{\rm uc}$ (sb/lb) (E_h)	$\left(E^{\rm PATMOS,eff}_{\rm uc} - 2E^{\rm PATMOS}_{\rm atom}({\rm isolated})\right)/2$ (E_h)
3	3	0.009435	-0.000438	-0.001246	0.007752	-0.019651
5	5	0.003138	-0.000125	-0.000268	0.002742	-0.022156
7	7	0.001348	-0.000071	-0.000131	0.001146	-0.022954
9	9	0.000654	-0.000024	-0.000053	0.000576	-0.023239
11	11	0.000320	-0.000011	-0.000028	0.000280	-0.023388
13	13	0.000124	-0.000005	-0.000012	0.000106	-0.023474
15	15	0.0	0.0	0.0	0.0	-0.023527
		(-14.897549)	(-0.078801)	(-0.016670)	(-14.993022)	

TABLE VI. Binding energies per lithium atom using two different large basis sets. Unit cell dimension $r_{\rm uc} = 2r_{\rm Li1,Li2} = 10.0$ bohr, on the repulsive branch of the potential energy curve, and model parameters $N^{\rm uc}_{\rm model} = N^{\rm uc}_{\rm bf} = 7$.

Basis sets		$\Delta E = \left(E^{\rm PATMOS,eff}_{\rm uc} - 2E^{\rm PATMOS}_{\rm atom}({\rm isolated})\right)/2$
sb	*lb*	(E_h)
$11s2p$	$15s7p2d1f$	0.019987
$11s2p$	$19s8p7d5f2g1h$	0.020273

Figure Captions

Figure 1: Model of infinite, one-dimensional periodic system of unti cells.

Figure 2: Intersection between the xy-plane and the charge ellipsoids of α- and β-type orbitals of the atoms in the reference cell of the one-dimensional array of H atoms. The number of unit cells in model and the number of unit cells in the basis function region are respectively $N^{\rm uc}_{\rm model} = 13$ and $N^{\rm uc}_{\rm bf} = 13$. Half axes and distance in scale. Basis: $(sb/lb) = (10s2p1d/13s4p3d1f)$.

Figure 3: Intersection between the xy-plane and the charge ellipsoids of the valence α- and β-type orbitals in the reference cell of the one-dimensional array of Li atoms. The number of unit cells in the model and the number of unit cells in the basis function region are respectively $N^{\rm uc}_{\rm model} = 13$ and $N^{\rm uc}_{\rm bf} = 13$. Half axes and distance in scale. Basis: $(sb/lb) = (11s2p/15s7p2d1f)$.

Figure 1, Inge Røeggen et al, J. Chem. Phys.

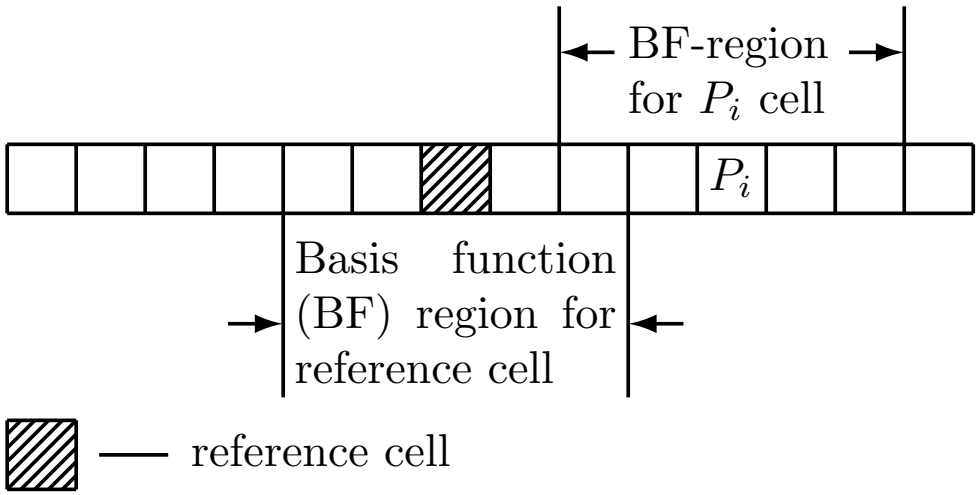

Figure 2, Inge Røeggen et al, J. Chem. Phys.

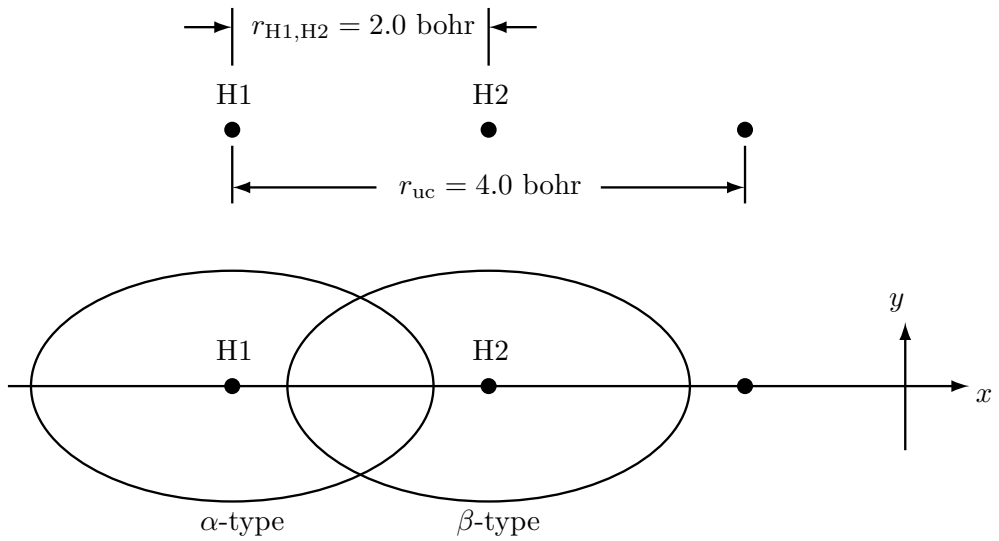

Figure 3, Inge Røeggen et al, J. Chem. Phys.