Abstract

An approximative method for solving the Bloch-Torrey equation in general porous media is presented. The method expands the boundaries defining the porous media using electrostatic charges. As a result, the eigenvalue problem of the Laplace operator in a confined geometry can be approximately solved. Importantly, the approximative solution is orthogonal in the low-frequent region of Fourier space. This gives a natural approach for studying spin magnetization in the presence of magnetic fields. The error in the approximation scales with $N^{-2}$ times the magnitude of each eigenvalue, where $N$ is the size of the expansion matrix. From a computational point of view, the calculations scale quadratically with the number of basis functions using fast multipole methods.

Nuclear Magnetic Resonance (NMR) provide an excellent tool for directly studying transport properties in porous media as well as indirectly study the porous media itself [1, 2, 3]. Geometrical properties such as surface-to-volume ratio [4, 5, 6], characteristic length scales [7, 8, 9] and pore size distributions [10, 11, 12, 13] has successfully been derived. The analysis of the experimental signal is however in many cases difficult as [14, 15]. The main reason is that a theoretical analysis of the NMR experiment in porous media is difficult [15]. A diffusing spin in a porous media is described by the Bloch-Torrey equation [16]. Analytic solutions exist only for a few simple geometries and for general media clues may be found from numerical simulations. Another reason for the difficulty in analysing the experiments lie in the fact that the experimental conditions for the theoretical models available cannot always be met, e.g. that the time for the gradient is short enough for the so-called short gradient pulse limit to hold [17, 18, 19]. Therefore, an analysis of the experimental signal is often done using clues from simple geometries crude models. It is possible to view this experiment as probing a porous media with low-frequent Fourier modes, and study the response. In the SGP-limit this aspect is in fact exact, as the experimental signal is the Fourier...
transform of the diffusion propagator in a porous media. If no boundaries are present, the Fourier modes stay orthogonal, and the experimental signal is just the exponent of the fourier wave number times the experimental time. If however the media is not free, the Fourier modes get mixed as they pass through the media, and the experimental response show this mixing. Therefore it would be advantegeous to study this mixing, as it reveal information about the geometry of the porous media.

In this paper an approximate method is presented that connects a general porous media with the associated eigenspectrum of the Laplace operator and the magnetic resonance experiment. Importantly this gives the possibility of directly studying the geometrical impact on NMR diffusometry experiments in more complex porous media.

The Bloch-Torrey equation describes a diffusing spin in a porous media subject to an external magnetic field. For simplicity we assume that the self-diffusion is isotropic and the following equation is obtained [ref price, Barzykin]

\[
\dot{m}(r, t) = \left( D_0 \Delta + i \gamma f(t) G(r) \right) m \quad r \in \Omega \\
(a \frac{\partial}{\partial n} + b) m(r, t) = 0 \quad r \in \Gamma
\] (1)

where \(D_0\) denote the self diffusion coefficient, \(\gamma\) the gyromagnetic ratio and \(f(t)\) a time profile of the gradient and \(G(r)\) a magnetic field gradient which can include also internal gradients. The sought complex valued function \(m\) describes the magnetization.

In the case of a freely diffusing spin, the diffusion can easily be solved by diagonalizing the heat kernel and the resulting effect of the spin for a given diffusion time \(t\) will be dominated by the eigenfunctions corresponding to the eigenvalues smaller than \(e^{-t\lambda_n}\) for some largest \(n\). In other words, the diffusive motion a spin undergoes during time \(t\) will be dominated by the low-frequent eigenfunctions up to a certain truncation. The shorter time, the more functions are needed. It is tempting to think that a similar analysis can be made also in the case of a spin diffusing in a porous media. This equation can be solved by formally integrating the magnetization in time (see e.g. [19]) and expressing the solution in the eigenbasis of the Laplace operator.

\[
m(r, t) = e^{-i(D_0 \Delta + i f G) t} m(r, t = 0).
\] (2)

It can also be solved by exploring the solution in Fourier space [20]

\[
\frac{\partial \hat{m}(q, t)}{\partial t} = \gamma f(t) FT[iG(r)] - D_0 q^2 \hat{m}(q, t).
\] (3)

This approach is appealing, as in absence of boundaries the Fourier modes satisfy the Laplace operator. The problem here is however that when boundaries are present, the Fourier transformed magnetization is difficult to solve. One may however note that if such a transformation is found, the averaged signal is found by the limit [20]

\[
m(t) = \lim_{q \to 0} \hat{m}(q, t).
\] (4)

The problem stated in Eq. 1 can be solved by calculating the eigenfunctions and the eigenvalues to the Laplace operator in the confined domain \(\Omega\). This can be stated as

\[
\begin{align*}
\Delta u_n(r) &= \lambda_n u_n(r) \quad r \in \Omega \\
(\frac{\partial}{\partial n} + a) u_n &= 0 \quad r \in \Gamma
\end{align*}
\] (5)

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where the porous material is defined by the boundary conditions at $\Gamma$.

Let us define the following integral operators to represent the boundary conditions. For Dirichlet conditions at $\Gamma$

\[
af \mid_\Gamma = \int_\Gamma \delta(r - r_0) f(r_0) dr_0 = \begin{cases} 
af(r) & \text{if } r \in \Gamma \\
0 & \text{if } r \in \Omega \setminus \Gamma
\end{cases}
\]  

where $\delta$ denote the Dirac-delta function. The corresponding operator for Neuman conditions is defined as

\[
\frac{\partial}{\partial n} f \mid_\Gamma = \int_\Gamma (\hat{n}(r_0) \cdot \nabla) \delta(r - r_0) f(r_0) dr_0 = \begin{cases} 
\hat{n} \cdot \nabla f(r) & \text{if } r \in \Gamma \\
0 & \text{if } r \in \Omega \setminus \Gamma
\end{cases}
\]  

where $(\hat{n}(r_0) \cdot \nabla) \delta(r - r_0)$ denote the distributional derivative of the Dirac-delta function directed along the normal of the boundary $\Gamma$ at $r_0$. Using these, we can define the following inner product for two functions $f$ and $g$

\[
\langle f \mid \frac{\partial}{\partial n} + a \mid g \rangle_\Omega = \int_\Omega f(r) \int_\Gamma (\nabla \cdot \hat{n}(r') \delta(r - r') + a \delta(r - r')) g(r') dr' dr = \\
= \int_\Gamma f(r)(\hat{n}(r) \cdot \nabla + a) g(r) dr
\]  

which we may note is zero if the function $g(r)$ satisfies the boundary conditions. Note that if a function $u(r)$ satisfies Eq. 5 then it is also satisfying the boundary conditions in Eq. 5 and can be written as a linear combination of the sought eigenfunctions $\{u_n\}_{n=1}^\infty$ in Eq. 5.

In absence of the internal boundary conditions $\Gamma$ a general function $f(r \in \Omega)$ can be written as a linear combination of Fourier modes $f(r \in \Gamma) = \sum_{n=1}^\infty a_n |q\rangle$. These Fourier modes satisfy Eq. 5 without the boundary conditions at $\Gamma$. This can be written as

\[
\Delta |q\rangle = \lambda_q |q\rangle
\]  

where the eigenvalues $\lambda_q$ are analytic and given by the exterior boundary conditions (Dirichlet, Neumann or periodic) at $\Omega$. In example for the case of Dirichlet exterior boundary conditions with $\Omega$ being a box of side length $L$ the functions $|q\rangle$ equal

\[
|q\rangle = A_q \sin(n_x \pi x L) \sin(n_y \pi y L) \sin(n_z \pi z L)
\]  

where $A_q$ is the normalization constant. The corresponding eigenvalues equal

\[
\lambda_q = \frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2).
\]  

We expect that it is possible to expand each eigenfunction of Eq. 5 using the set $\{|q\rangle\}_{q=1}^\infty$ i.e. Fourier transforming the eigenfunctions. The problem with this approach
is that the eigenfunctions satisfying Eq. 5 are not local in Fourier space, meaning that a perturbation expansion of the eigenfunctions into the set \( \{|q\rangle\}_{q=1}^{\infty} \) give poor convergence. The reason is that there is a reciproc relationship between the boundaries at \( \Gamma \) in Eq. 5 and the Fourier space on \( \Omega \). It would however be of great advantage if one could find the low frequent behaviour of the solution to Eq. 5 in Fourier space as this set has an intimate relationship with the calculation of the magnetization in NMR diffusometry (explained below).

It is a well-known fact (see e.g. [21, 22, 23]) that given an eigenvalue \( \lambda_n \) to Eq. 5 there exists a corresponding surface distribution \( f_n(r \in \Gamma) \) such that the following inhomogeneous Helmholtz problem is satisfied

\[
\Delta u_n(r \in \Omega \cup \Gamma) = (\Delta - \lambda_n I)^{-1} f_n(r \in \Gamma). \tag{13}
\]

This can be seen by rewriting Eq. 13

\[
\Delta u_n - f_n = \lambda_n u_n \tag{14}
\]

and letting the function \( f_n \) equal

\[
f_n = (\frac{\partial}{\partial n} + a)|\Gamma| u_n. \tag{15}
\]

This reviel a source term \( f_n \) that can be viewed as inducing the boundary conditions in equation 5 and is a well explored concept in potential theory[24]. For Neumann conditions \( f_n \) consist of dipoles and for Dirichlet conditions it consist of monopoles. By using the identity

\[
(Q + P)^{-1} = Q^{-1} - Q^{-1}P(Q + P)^{-1} \tag{16}
\]

together with Eq. 13 the following integral equation is found

\[
u_n = \Delta^{-1} f_n + \lambda_n\Delta^{-1}(\Delta - \lambda_n I)^{-1} f_n. \tag{17}
\]

Let us for a moment assume that the exterior boundary (\( \Omega \)) is infinitely large and investigate the second term in Fourier space. Let us denote the transform vector by

\[
|q\rangle = |q_x q_y q_z\rangle = e^{i(q_x \hat{x} + q_y \hat{y} + q_z \hat{z}) \cdot r}. \tag{18}
\]

We get

\[
\lambda_n \int_{-\infty}^{\infty} dq |q\rangle \langle q| \Delta^{-1}(\Delta - \lambda_n I)^{-1} |f_n\rangle = \lambda_n \int_{-\infty}^{\infty} dq |q\rangle |\Delta - \lambda_n I|^{-1} |f_n\rangle \frac{|q|}{||q||^2}. \tag{19}
\]

The inverse to the Helmholtz operator in Eq. 19 can be directly evaluated in Fourier space. A fundamental solution to the Helmholtz operator \( G(r, r_0, \kappa) \) satisfy
\( (\Delta - \kappa^2 I)G(r, r_0, \kappa) = \delta(r - r_0) \)  

in any dimension. Fourier transforming equation 20 yield

\[
\tilde{G}(q, r_0, \kappa) = \frac{1 - e^{-i r_0 \cdot q}}{(\kappa^2 - \|q\|^2)} e^{-i r_0 \cdot q} \quad \text{for } \|q\| \gg |\kappa|.
\]

Hence the result of introducing two (separated) charges merely introduces a modulation of the solution in Fourier space, with a frequency associated to the separation of the charges. It is thus concluded that the Fourier expansion in equation 19 is local around \( \kappa^2 \) and that this holds regardless of the number of sources and positions of the sources. In other words regardless of the shape of the boundary \( \Gamma \). This also hold in the case where exterior boundary conditions are imposed (by analysis of Fourier series). The second term in Eq. 19 can thus be truncated to the following expression

\[
\cdots \approx \frac{\lambda_n}{\|q\|^2} \int_{-|\lambda_n|+C}^{|\lambda_n|+C} dq \frac{|\langle q | (\Delta - \lambda_n I)^{-1} | f_n \rangle \| q \|^2}{|\lambda_n|^2} + \lambda_n O(\lambda_n^{-2} |\lambda_n|^{-2})
\]

for some scalar \( C \). Eq. 19-23 involve the free-space Helmholtz operator. The original eigenvalue equation is bounded in a domain, typically Neumann, Dirichlet or a periodic. The inverse to the Helmholtz operator in such domains will also be local in Fourier space and have the same asymptotic behavior (Neumann, Dirichlet or periodic conditions give a subset of the free space operator in Fourier space). The equivalent of Eq. 24 for such domains is a truncated Fourier series expansion

\[
\tilde{u}_n \approx \sum_{q=1}^{N} |q\rangle \langle q| (\Delta - \lambda_n I)^{-1} | f_n \rangle + \sum_{q=1}^{N} \frac{|q\rangle \langle q| (\Delta - \lambda_n I)^{-1} | f_n \rangle}{|\lambda_n|} + O(|\lambda_n|^{-2})
\]

for some \( N \). On such a domain (Dirichlet) one has

\[
\delta(r) = \frac{1}{2\pi} \sum_{q=\infty}^{\infty} e^{iqr}
\]

Let us now assume that the correct surface distribution \( |f_n\rangle \) satisfying Eq. 17 is unknown. This can be formulated in the following way:
Given a boundary $\Gamma$ we seek a correct surface distribution $|f_n(\mathbf{r} \in \Gamma)\rangle$ such that when plugged in equation (25) yield the correct sought eigenfunction $u_n$. This can be solved by using a (any complete) series expansion over the boundary $\Gamma$. A harmonic expansion is suitable \cite{17} (but probably not optimal)

$$|f_n\rangle = \sum_{\sigma=0}^{\infty} |\sigma\rangle \langle \sigma|f_n\rangle = \sum_{\sigma=0}^{\infty} \beta_{\sigma n} |\sigma\rangle.$$  

(27)

Combining equation 27 with equation 25 we get

$$\tilde{u}_n \approx \sum_{\sigma=1}^{\infty} \sum_{q=1}^{\infty} \beta_{\sigma n} |q\rangle\langle \sigma| \Delta^{-1} |\sigma\rangle + \sum_{\sigma=1}^{\infty} \sum_{q=1}^{N} \beta_{\sigma n} |q\rangle \langle q| \left(\Delta - \lambda_n I\right)^{-1} |\sigma\rangle + O(q^{-2}|\lambda_N|^{-2}).$$

(28)

The first term has poor convergence in Fourier space. An efficient solution to this problem is to construct an orthogonal complement to the set $\{|q\rangle\}_{q=1}^{N}$ using for Dirichlet conditions on $\Gamma$ the monopole kernel

$$|s\rangle = \int_{\Omega} \frac{\sigma(r')\hat{n}(r')}{||r-r'||} dr'.$$

(29)

and in the case of Neumann conditions the dipole kernel

$$|s\rangle = \int_{\Omega} \frac{\sigma(r')\hat{n}(r')}{||r-r'||^2} dr'.$$

(30)

Then an orthogonal series can be constructed using the expansion of the surface expansion $\{|\sigma\rangle\}_{\sigma=1}^{\infty}$ in the following way

$$|s_1\rangle = \Delta^{-1}|\sigma = 1_n\rangle.$$

$$|s_k\rangle = \Delta^{-1}|\sigma = k_n\rangle - \sum_{j=1}^{k-1} |s_j\rangle \langle s_j| \Delta^{-1} |\sigma = k_n\rangle - \sum_{j=1}^{N} |q_j\rangle \langle q_j| \Delta^{-1} |\sigma = k_n\rangle$$

$$\vdots$$

for $k \rightarrow \infty$.

By this, a mixed basis is obtained

$$\{|q = 1\rangle, |q = 2\rangle, \ldots, |q = N\rangle, |s = 1\rangle, |s = 2\rangle, \ldots, |s \rightarrow \infty\rangle\}.$$  

(31)

It is a straight forward excercise to show that the constructed infinite series $\{|s_1\rangle, |s_2\rangle, \ldots\}$ span a strict subspace of the function space in the joint domain $\Omega \cup \Gamma$. In fact $\{q\}_{q=1}^{N} \cup \{|s\rangle\}_{s=1}^{\infty}$ span approximately the first $N$ sought eigenfunctions $u_n$ (with an error $O(q^{-2}|\lambda_N|^{-2})$). Furthermore if one lets $N$ grow to infinity, the orthogonal set $\{|s\rangle\}_{s=1}^{\infty}$ is forced to the null-space by its construction i.e. the mixed basis is not over-determined (it is however not complete, by the truncation). Therefore one may choose a truncation $N$ and
effectively capture the low-frequent behaviour of the Laplace operator in a bounded domain.

Returning to the original problem Eq. 5 where the eigenvalues \( \lambda_n \) and eigenfunctions \( u_n \) are unknown, a perturbation matrix \( A \) using the mixed basis in Eq. 33 can be formed which captures the relevant low-frequency information of the eigenproblem stated in Eq. 5 in the following way

\[
A_{nm} = \begin{cases} 
\langle q_n | \Delta | q_m \rangle_\Omega - \langle q_n | (\frac{\partial^2}{\partial n^2} + \alpha) | q_m \rangle_\Gamma & \text{if } n, m \leq N \\
\langle q_n | \Delta | s_m \rangle_\Omega - \langle q_n | (\frac{\partial^2}{\partial n^2} + \alpha) | s_m \rangle_\Gamma & \text{if } n \leq N < m \\
\langle s_n | \Delta | q_m \rangle_\Omega - \langle s_n | (\frac{\partial^2}{\partial n^2} + \alpha) | q_m \rangle_\Gamma & \text{if } m \leq N < n \\
\langle s_n | \Delta | s_m \rangle_\Omega - \langle s_n | (\frac{\partial^2}{\partial n^2} + \alpha) | s_m \rangle_\Gamma & \text{if } N < n, m
\end{cases}
\]

(32)

where the subscript \( \Gamma \) is a reminder of the fact that the inner products are calculated on the boundaries only using Eq. 8. Let us take a moment and look at the integrals involving the boundary conditions. The first term involving \( q_n, q_m \) is easily evaluated using Eq. 8. The integrals involving the surface functions are however a bit more subtle, due to the infinities of the potentials at the origin of the charges. We get using (Eq. 8)

\[
\langle q_n | (\frac{\partial}{\partial n} + \alpha) | s_m \rangle_\Gamma = \int_\Gamma q_n(r) (\hat{n}(r) \cdot \nabla + \alpha) s_m(r) \, dr = \int_\Gamma q_n(r) (\hat{n}(r) \cdot \nabla + \alpha) \frac{\sigma_m(r')}{||r - r'||} \, dr' \, dr
\]

(33)

\[
= \int_\Gamma q_n(r) (\frac{\partial}{\partial n} + \alpha) \frac{\sigma_m(r')}{||r - r'||} \, dr' \, dr.
\]

(34)

Now we split the rightmost integral in two parts

\[
\int_\Gamma (\frac{\partial}{\partial n} + \alpha) \frac{\sigma_m(r')}{||r - r'||} \, dr' = \Phi_0(r) + \Phi_1(r)
\]

(35)

where \( \Phi_0 \) is the potential from the charges located at the position of \( r \) (self-interaction) and \( \Phi_1 \) is the potential arising from surrounding charges. Evidently \( \Phi_1 \) is finite. For \( \Phi_0 \) we get (in the case of Neumann)

\[
\hat{n} \cdot \nabla \Phi_0 \to \infty
\]

(36)

but importantly this only evaluated at \( \Gamma \) (and is symmetric across the boundary) and therefore efficiently acts as a \( \delta \)-function. Therefore

\[
\int_\Gamma q_n(r) \hat{n} \cdot \nabla \Phi_0(r) \, dr = C \int_\Gamma \sigma_m(r) \hat{n} \cdot \nabla q_n(r) \, dr
\]

(37)

for some constant \( C < \infty \). The \( \Phi_1(r) \) contribution is evaluated as

\[
\int_\Gamma q_n(r) \hat{n} \cdot \nabla \Phi_1(r) \, dr = \int_\Gamma q_n(r) \hat{n}(r) \cdot \nabla \int_\Gamma \hat{n}(r') \cdot \nabla \frac{\sigma_m(r')}{||r - r'||} \, dr' \, dr \quad (r \neq r')
\]

(38)
\begin{align*}
&= \int_{\Gamma} q_n(r) \hat{n}(r) \cdot \nabla \Phi_1(r) = - \int_{\Gamma} q_n(r) \hat{n}(r) \cdot F(r) dr \tag{39} \\
&= - \int_{\Gamma} dq_n(r) \hat{n}(r) \cdot d\sigma \left( \frac{3\hat{n}(r') \cdot \hat{a}}{||r-r'||^3} - \frac{\hat{n}(r')}{||r-r'||^3} \right) \tag{40}.
\end{align*}

where \( \hat{a} = (r-r')/||r-r'|| \) is the unit vector pointing from \( r \) towards \( r' \). which effectively gives the force due to surrounding dipoles along the boundary \( \Gamma \). This can be interpreted as calculating the work needed to move a charged particle along \( \Gamma \) subject to the field emerging from a dipole distribution. This can be calculated for each individual dipole and the total contribution can be found by integration. Note that if the surface is smooth, the function behaves (relatively) nice, as the scalar product disappears in case of a flat surface. The products

\[ \langle s_n | \left( \frac{\partial}{\partial \hat{n}} + a \right) | s_m \rangle \Gamma \]

are evaluated in a similar way. Together with a orthogonalization matrix

\[ B_{nm} = \begin{cases} 
\delta_{nm} & \text{if } n, m \leq N \\
\langle q_n | s_m \rangle \Omega & \text{if } n \leq N < m \\
\langle s_n | q_m \rangle \Omega & \text{if } m \leq N < n \\
\langle s_n | s_m \rangle \Omega & \text{if } N < n, m 
\end{cases} \tag{42} \]

an approximation to the \( N \) first eigenvalues and eigenfunctions to the eigenproblem is found by diagonalizing the orthogonalization matrix \( B \)

\[ VDV = B \tag{43} \]

and thus forming a basis transformation \( W \)

\[ W = V \sqrt{D}^{-1} \tag{44} \]

which can be used to diagonalize

\[ V_A D_A V_A = W^T A W \tag{45} \]

\( D_A \) then contain an approximation to the \( N \) first eigenvalues of the eigenproblem, and an approximation to the corresponding \( N \) first eigenfunctions (in the mixed basis) can be read out by the columns of \( V_A \). Furthermore, in the low-frequent domain the eigenfunctions are expected to vary slowly also locally to the boundaries. Therefore in practice, the surface expansion \( \left\{ | \sigma \rangle \right\}_{\sigma=1}^\infty \) can be truncated to a finite value \( \left\{ | \sigma \rangle \right\}_{\sigma=1}^M \). In fact, this value is expected to be quite low since the variation of all possible surface modes \( | \sigma \rangle \) on \( \Gamma \) is smeared out to small variations in the volume \( \Omega \) by the integral operator \( \Delta^{-1} \). The analysis of the truncation of the surface expansion is left out in this study with the comment that previous numerical studies show that in practice a low number \( M \) yield good results (see e.g. \[17\]). Previously [17] it has also been shown that all inner products in 32-42 can be transformed to surface integrals using the self-adjointness of the Laplace operator and the following two relations
\[ \Delta |q\rangle = \lambda q |q\rangle \]
\[ \Delta |s\rangle = |\sigma_s\rangle. \]

A few more useful insights are reported. For Neumann conditions the charge distributions \(|\sigma\rangle\) consist of dipole distributions. In this case the inner product of the resulting potentials appearing in Eq. (42) can be evaluated on the surface in the following way
\[
\langle s_n|s_m\rangle = \begin{cases} \int \int drdr' \sigma_n(r)\sigma_m(r') \frac{\hat{a}(r)\hat{a}(r')}{||r-r'||} & \text{in the case of Dirichlet conditions on } \Gamma \\ \int \int drdr' \sigma_n(r)\sigma_m(r') \frac{\hat{a}(r)\hat{a}(r')}{||r-r'||} & \text{in the case of Neumann conditions on } \Gamma \end{cases}
\]
(46)

A derivation of this result is attached as an appendix of this paper.

\[
|s\rangle = \int_{\Omega} \frac{\sigma_s(r')\hat{a}(r')}{||r-r'||^2} dr' \Rightarrow 
\langle s | x | s' \rangle = \int_{\Omega} x dr \int_{\Omega} \frac{\sigma_s(r')\hat{a}(r')}{||r-r'||^2} dr' \int_{\Omega} \frac{\sigma_s(r'')\hat{a}(r'')}{||r''-r'||^2} dr'' = 
\int_{\Omega} \sigma_s(r') \Xi_g(r',r'') \sigma_s(r') dr' dr''.
\tag{47}
\]

\[
\Xi = \int dr'' (g \cdot r'') \frac{\hat{a}(r')}{||r''-r'||^2} \frac{\hat{a}(r')}{||r''-r'||^2} = 
\pi |g \times \hat{a}(r,r')| \cdot [\hat{a}(r) \times \hat{a}(r')] \\
- \pi g \cdot \hat{a}(r,r') \left( [\hat{a}(r) \cdot \hat{a}(r')] \\
- [\hat{a}(r) \cdot \hat{a}(r')] [\hat{a}(r') \cdot \hat{a}(r')] \right)
\tag{48}
\]

where \( \hat{a} = \frac{r-r'}{||r-r'||} \) is the directional (unit) vector between \( r \) and \( r' \) and \( \hat{a} \) is the (outward) pointing normal at the boundary \( \Omega \). A few comments on the result are appropriate. If the eigenbasis of the kernel appearing in Eq. (46) is found, orthogonal surface functions can be constructed directly. This is realized by letting the set \( \{\sigma_n\}_{n=1}^\infty \) equal the eigenbasis of \( \Theta \) i.e. \( \langle \sigma_n|\Theta|\sigma_m\rangle = \delta_{nm} \lambda_m \) where \( \lambda_m \) equal the eigenvalue of \( \Theta \) corresponding to the eigenfunction \( |\sigma_m\rangle \). In example: A special case is found when the surface is flat (independent of the scalar product between the surface normals). The kernel \( \Theta \) then reduces to the Poisson kernel and the eigenfunctions are analytically known. Similar simple expressions are expected from simple domains such as spheres, cylinders et cetera. Importantly this introduces the possibility of filling a space with such bodies and solve approximately the eigenvalue problem as well as the Bloch-Torrey equation in the void space between the bodies in a mesh-free way with the above approach. The demanding computational step is then to find the electrostatic potentials between such bodies. This is a standard problem and solutions using fast multipole methods have
been proposed [25, 26, 27]. Furthermore non-trivial bodies could be approximated by discrete grids. This would yield a finite set of surface functions. A harmonic expansion on such surfaces could easily be constructed by mapping the spherical harmonics to such bodies and it is expected that few such functions are needed for good results. It has been shown that such calculations can be performed in optimal time with respect to the number of discretation points on the surfaces. On a computational note, the kernel in Eq. 46 is symmetric and problem independent. It can thus be calculated off-line and in an implementation interpolation can be made using the distance between the surface elements and the scalar product between the surface normals.

Appendix: Derivation of the dipole kernel

For the mixed basis to make sense, it must be orthogonalized before the perturbation matrix is formed (for details, see [28, 17]). In particular this require the inner product between the surface functions \( \langle s | s' \rangle \) which are defined throughout the whole volume. These inner products can be transformed to surface integrals and here follows a derivation of this result. The surface functions are defined as solutions to the inhomogeneous Poisson’s equation

\[
|s\rangle = \int_{\Omega} \frac{\sigma_s(r')\hat{n}(r')}{||r-r'||^2} \, dr'
\tag{49}
\]

where \( \sigma_s \) denote a dipole distribution at the surface and \( \hat{n} \) the (outward) pointing surface normal and the kernel is the fundamental solution for a dipole potential [29]. Typically we want to express the surface contributions of \( S \) by a function expansion on the surface. Since the \( S \)-operator is located to the boundaries and thus has a huge null-space more or less any truncated function expansion on the surface will capture the low frequency part of the (volume) contribution. The reason for this is that the null-space is known trivially. A Fourier expansion on the surface is suggested as the low frequency part is well captured by the first \( M \) Fourier functions on the surface. The (volume) inner products are formally written as

\[
\langle s_n(r)|s_m(r) \rangle = \int_{\Omega} \int_{\Omega} \frac{\hat{n}(r') \cdot r \sigma_n(r')}{||r-r'||^2} \, dr' \int_{\Omega} \frac{\hat{n}(r''') \cdot r \sigma_m(r''')}{||r-r''||^2} \, dr''dr'.
\tag{50}
\]

Where the outer integral is the volume integral. The convergence of the Poisson dipole kernel ensure us that we can interchange the order of integration, this results in

\[
= \int_{\Omega} \int_{V} \frac{\hat{n}(r') \cdot r \sigma(r') \hat{n}(r''') \cdot r \sigma(r''')}{||r-r'||^2} \, dV \, dr' \, dr''
= \int_{\Omega} \sigma(r') \sigma(r''') \Theta(r', r''') \hat{n}(r') \cdot \hat{n}(r''') \, dr' \, dr''
\]

10
where the kernel $\Theta$ is defined as
\[
\Theta(r', r'') = \int \frac{\hat{n}(r') \cdot r \cdot \hat{n}(r'') \cdot r}{||r - r'||^2 ||r - r''||^2} dV.
\] (51)

A multipole expansion of the potential from a dipole located in origo can be written as [29]
\[
\Phi_0(x) = \frac{1}{4\pi\varepsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} q_{lm} Y_{lm}(\theta, \phi) r^l + 1.
\] (52)

Let us denote the dipole by $p_0 = \hat{n}(0)d$ (and ensure that it is charge neutral). The scalar factors in equation 52 are found by
\[
q_{lm}^0 = \int Y_{lm}^*(\theta, \phi) r^l \rho_0(x) d^3x
\] (53)
where $\rho_0$ denotes the charge distribution. The only surviving terms in equation 53 are the dipole moments
\[
q_{11}^0 = -\sqrt{3} \frac{8\pi}{d} (p_{0x} - ip_{0y})
q_{10}^0 = \sqrt{3} \frac{4\pi}{d} p_{0z}
q_{1-1}^0 = -q_{11}^*
\] (54)
where $i$ denote the imaginary unit. For the second dipole located in the z-axis $p_1 = \hat{n}(a\hat{z})d$ not only the dipole moment survives but also higher modes. The potential from this dipole $\Phi_1(x)$ can still be expanded around origo as
\[
q_{00}^1 = 0
q_{11}^1 = -\sqrt{3} \frac{8\pi}{d} 2d \sin \theta_1 [\cos \phi_1 - i \sin \phi_1]
q_{10}^1 = \sqrt{3} \frac{4\pi}{d} 2d \cos \theta_1
q_{12}^1 = 0
q_{21}^1 = -\sqrt{15} \frac{8\pi}{d} 2ad \sin \theta_1 [\cos \phi_1 - i \sin \phi_1]
q_{20}^1 = \frac{1}{2} \sqrt{5} \frac{8\pi}{d} 8ad \cos \theta_1
\] (55)

We are interested in calculating
\[
\langle \Phi_0, \Phi_1 \rangle = \int \Phi_0(r) \Phi_1(r) dr = ...
\] (57)
and note that by the orthogonality of the spherical harmonics that the only surviving modes are the dipole modes

\[ ... = \left( \frac{1}{3\varepsilon_0} \right)^2 \left[ -q_{11}^0 q_{1-1}^1 + q_{10}^0 q_{10}^1 - q_{11}^0 q_{11}^1 \right] \int_a^\infty \frac{1}{r^4} r^2 dr = (58) \]

by evaluating the radial integral we get

\[ = p_0 \cdot p_1 \frac{1}{a}. \quad (59) \]

Since \( a \) is the distance between the two dipoles (and hence positive) we conclude

\[ \langle \Phi_0, \Phi_1 \rangle = \frac{p_0 \cdot p_1}{||r_0 - r_1||} = \hat{n}(r') \cdot \hat{n}(r'') = \Theta(r', r''). \quad (60) \]

Therefore, the (volume) inner product of two potentials \( \langle s | s' \rangle \) in equation \( 50 \) can be reduced to a (double) surface integral

\[ \langle s | s' \rangle = \int_\Omega \sigma_s(r') \sigma_s(r'') \Theta(r', r'') dr' dr'' . \quad (61) \]

A few comments on the result are appropriate. First, the kernel \( \Theta \) is symmetric and problem independent, it can thus be calculated off-line and in an implementation interpolation can be made using the distance between the surface elements and the scalar product between the surface normals. Secondly, this type of kernels can be approximated by single integrals using multipole methods. This has not yet been tested. Furthermore, if the eigenbasis of the kernel \( \Theta \) is found, orthogonal bases can be constructed directly. This is realized by letting the set \( \{ \sigma_s \}_{s=1}^M \) equal the eigenbasis of \( \Theta \) i.e. \( \langle \sigma_s | \Theta | \sigma_s' \rangle = \delta_{ss'} \lambda_s \), where \( \lambda_s \) equal the eigenvalue of \( \Theta \) corresponding to the eigenfunction \( |\sigma_s\rangle \). In example: A special case is found when the surface is flat (independent of the scalar product between the surface normals). The kernel \( \Theta \) then reduces to the Poisson kernel and the eigenfunctions are analytically known.

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